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Application of Fourier Transform Spectroscopy to Air Pollution Problems Computer-Generated Long-Path Air Spectra

Ohio State Univ Research Foundation, Columbus

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16 ABSTRACT

An atlas of computer-generated infrared transmission spectra of the atmosphere for low humidity (29 percent relative humidity) and high humidity (65 percent relative humidity) air samples is presented. These spectra extend from 700 cm^{-1} to 3000 cm^{-1}, and were computed with a resolution of approximately 0.25 cm^{-1}. The simulated path length is 3 km through an environment at 1013 mbar and 296 K.

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Interim Report - 1976
Computer-Generated Long-Path Air Spectra

by

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ABSTRACT

An atlas of computer-generated infrared transmission spectra of the atmosphere for low humidity (23 percent relative humidity) and high humidity (6 percent relative humidity) air samples is presented. These spectra extend from 700 cm^{-1} to 3000 cm^{-1}, and were computed with a resolution of approximately 0.25 cm^{-1}. The simulated path length is 3 km through an environment at 1013 mbar and 296 K.

INTRODUCTION

Analysis of high-resolution infrared spectra of long path lengths of air samples is a specific and highly sensitive technique for determining the presence of trace atmospheric gases. However, because of the presence of absorption lines of naturally occurring gases, especially H_2O throughout the region from 2-20 um, it is often difficult to identify features of trace pollutants unambiguously.

A number of techniques have been used to reduce the spectral interference due to the permanent gases. In one approach, spectra of air samples which are known to be "clean" are recorded and spectra of other samples are compared with these. This comparison can be accomplished very quickly if the absorption due to the permanent gases is nearly the same in both spectra and if the spectra are recorded digitally with data points of the spectral transmittance made at the same frequencies in each spectrum. Under these conditions, dividing one spectra transmission by the other will remove all of the absorption features which are the same in both spectra and leave only those features which differ. This technique is especially suitable for computer manipulation of data collected by the method of Fourier transform spectroscopy.

The principal requirements for this ratio method are that the spectral resolutions of both spectra be the same; that the temperatures, pressures and path lengths of both samples be the same; and that the composition of the background sample be known accurately. For most *in situ* applications of infrared spectroscopy, however, a background spectrum is difficult (if not impossible) to record. Fluctuations in the concentrations of CO, CO_2, and H_2O make the ratioing technique near the regions of their infrared bands ambiguous. Furthermore, if spectral features of a potential atmospheric contaminant are present in the background spectrum, the pollutant will not be observed in the ratioed spectrum.

An alternate technique to the direct method of ratioing is to perform a visual comparison of collected atmospheric transmission spectra to a spectrum which is calculated from the AFCRL Atmospheric Absorption Line Parameters Compilation.[1] This compilation, which is on magnetic tape, includes the vibration-rotation and pure rotation transitions of H_2O, O_3, CO, CO_2, CH_4, N_2O, and O_2. Pollutants are not included. Therefore, a spectrum of any desired path length through an unpolluted atmosphere can be calculated and used as a reference spectrum.

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[1] R.A. McClatchey, W.S. Benedict, S.A. Clough, D.E. Burch, R.F. Calfee, K. Fox, L.S. Rothman, and T. S. Garing, "AFCRL Atmospheric Absorption Line Parameters Compilation," AFCRL-TR-73-0096, Air Force Cambridge Research Laboratories Environmental Research Papers, No. 434 (1973).

There are several laboratory facilities where path lengths of 1.5 km or better can be obtained in multiple traversal cells. However, no path lengths in excess of 2 km of synthetic spectra of permanent atmospheric gases have been reported even though direct *in situ* measurements of 3 km are planned (P. Hanst, private communication) for a variety of urban atmospheric conditions.

This atlas of infrared transmission spectra is intended to be used in conjunction with actual long-path spectra. It is hoped that this atlas will not only help to reveal absorption features which may be due to other atmospheric constituents, but also will reveal inadequacies in the present knowledge of the absorption spectra of the permanent molecules in the atmosphere.

Two spectra have been compiled. The first spectrum represents the spectral transmission through a 3 km path length of air with a relative humidity of 39 percent (7970 ppm). The second spectrum represents the same path length through an atmosphere with a relative humidity of 65 percent (17,860 ppm). The concentrations of other atmospheric gases are listed in Table I. For both spectra the temperature was taken to be 296 K and the pressure was one atmosphere (1013 mbar).

TABLE I. Physical Parameters Used in Computation of Spectra

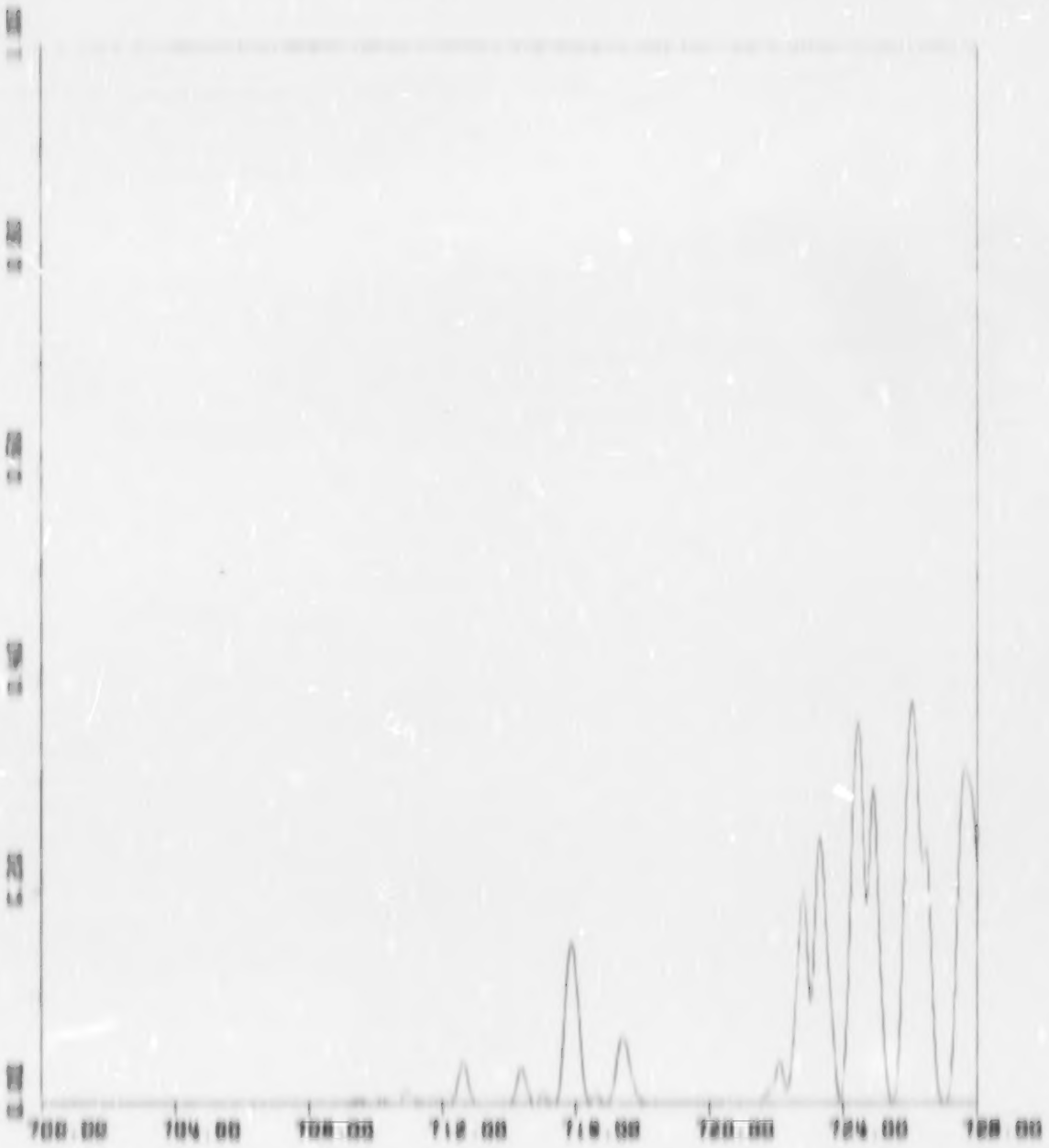
Pressure	= 1013 mbar
Temperature	= 296 K

Molecule	Concentration (by volume)	
CO_2	330	ppm
O_3	0.025	ppm
N_2O	0.27	ppm
CO	0.075	ppm
CH_4	1.6	ppm

Each page of this atlas shows a 25 cm^{-1} region. The two spectra are presented on facing pages, so comparison of the two spectra can be made easily. The low-water-vapor spectrum appears on the left hand pages. The spectra have a resolution of approximately 0.25 cm^{-1}. This was accomplished by first computing a spectrum with infinite resolution, and then numerically convolving this spectrum with a triangular slit function with a 0.25 cm^{-1} width. The atmosphere is opaque for 3 km path lengths in the spectral regions from 1375 cm^{-1} to 1600 cm^{-1} from 2275 cm^{-1} to 2375 cm^{-1} and these regions are not reproduced.

Synthetic spectra for shorter path lengths than these shown in this atlas are in excellent agreement with actual air spectra of similar path lengths. A compilation of actual and synthetic spectra of homogeneous paths up to 1 km and of slant path solar spectra is being prepared (Nordstrom *et al.*, in preparation).

This atlas of air spectra includes absorptions due to individual spectral lines up to 20 cm^{-1} from the line center. Continuum attenuation by H_2O absorption, aerosol absorption, and scattering have been neglected. Furthermore, the pressure-induced absorption by N_2 near 2500 cm^{-1} has also been neglected. For an actual atmospheric sample the fractional transmittances will be less than is shown in these spectra.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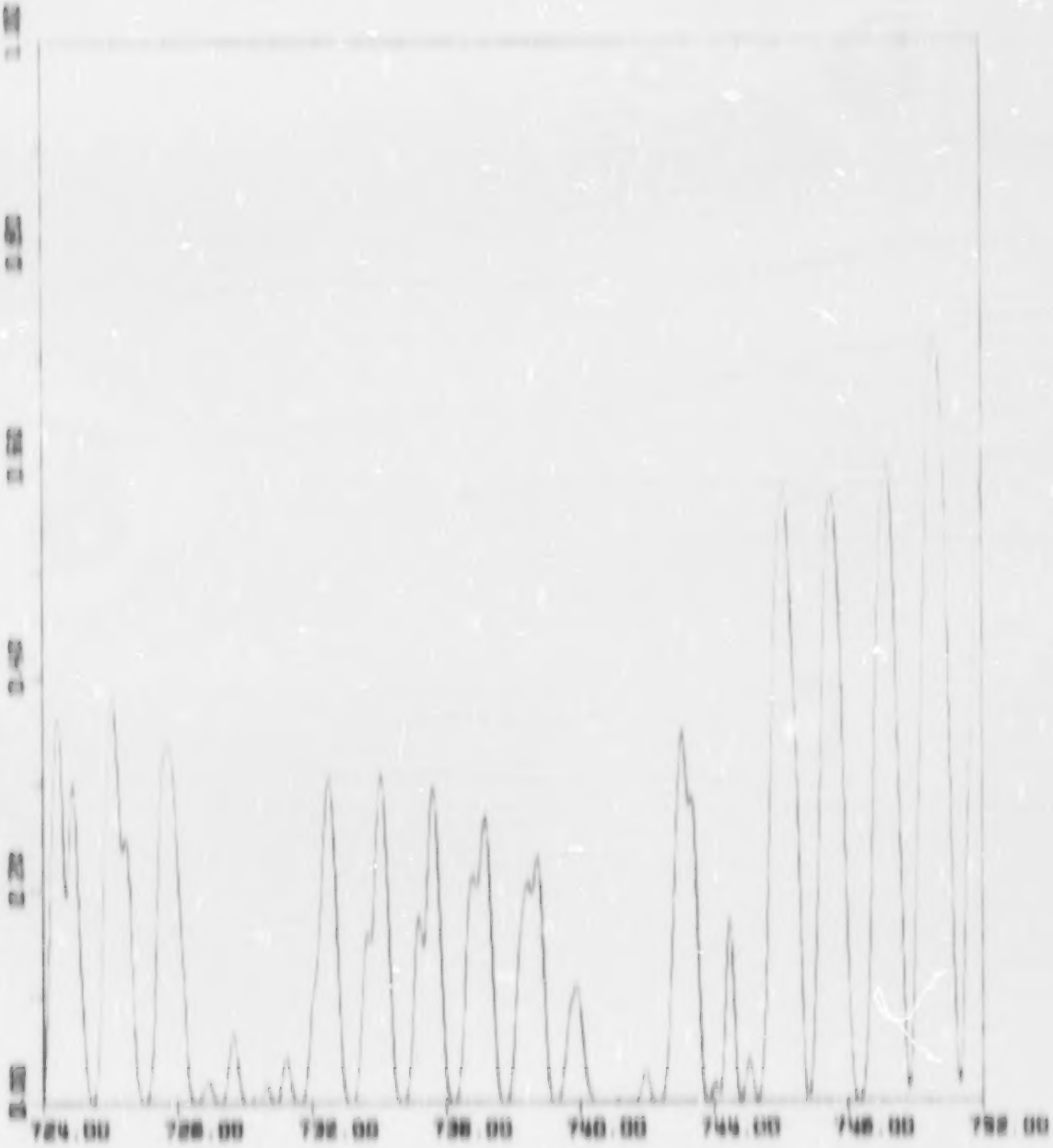
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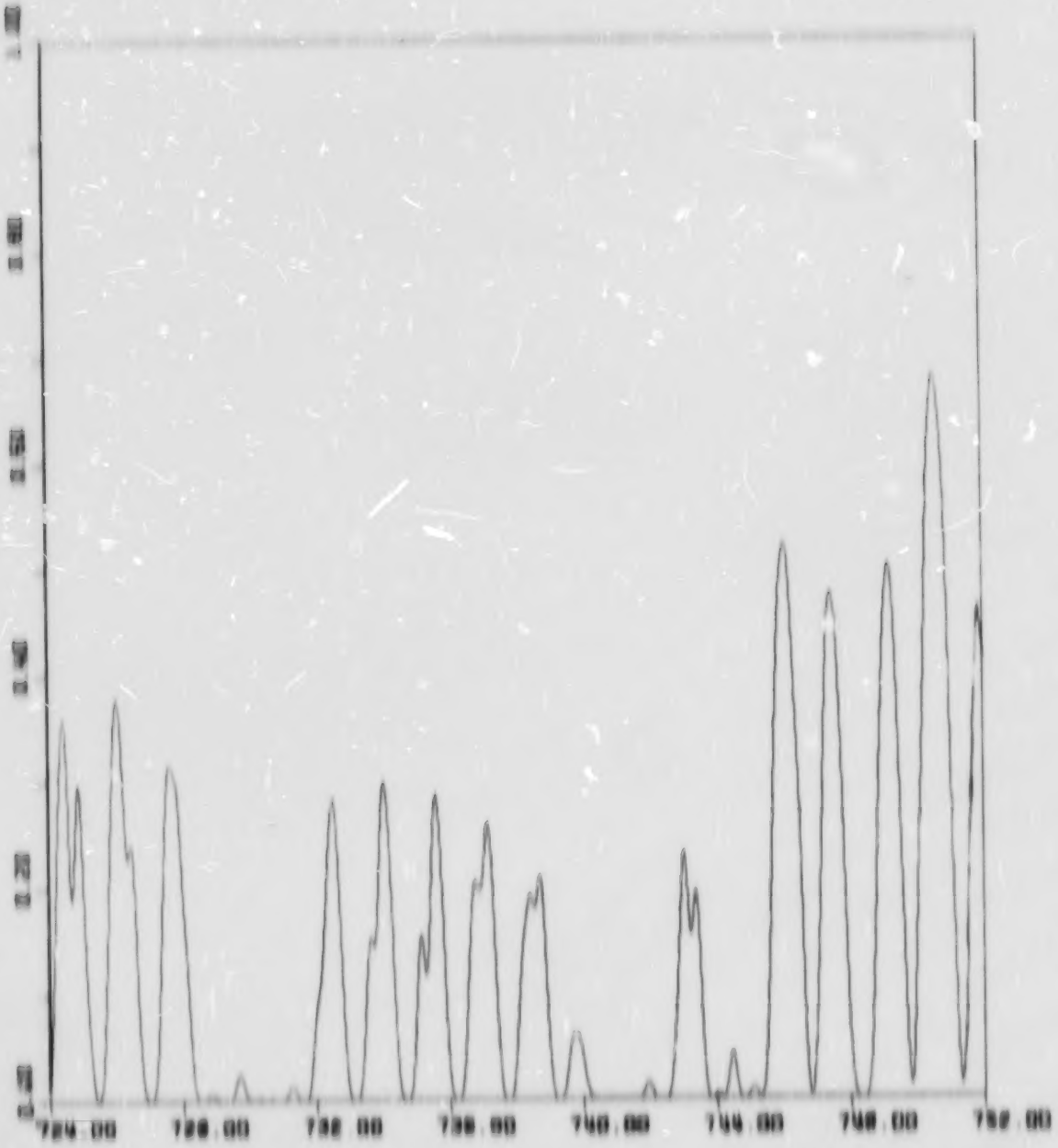
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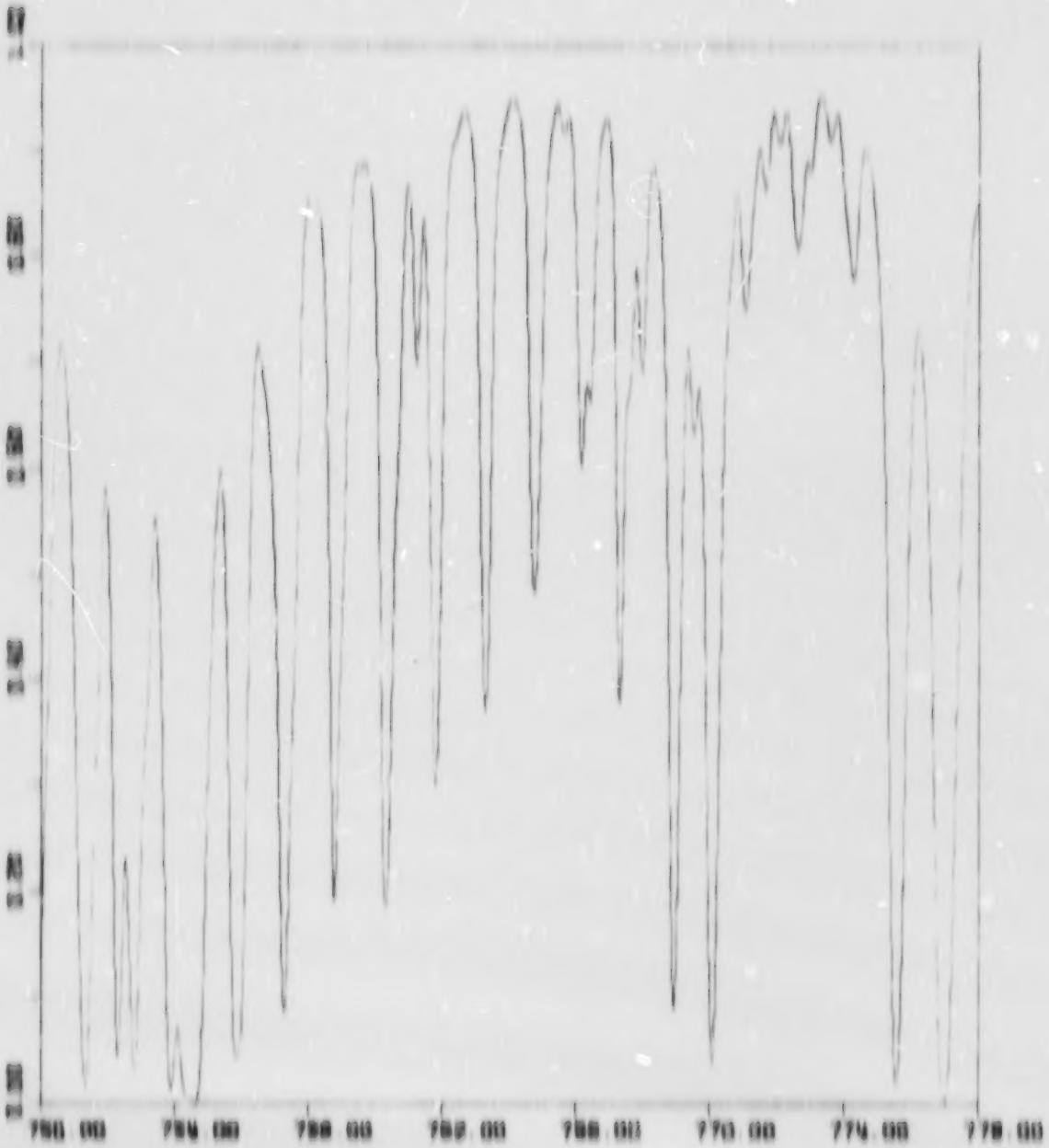
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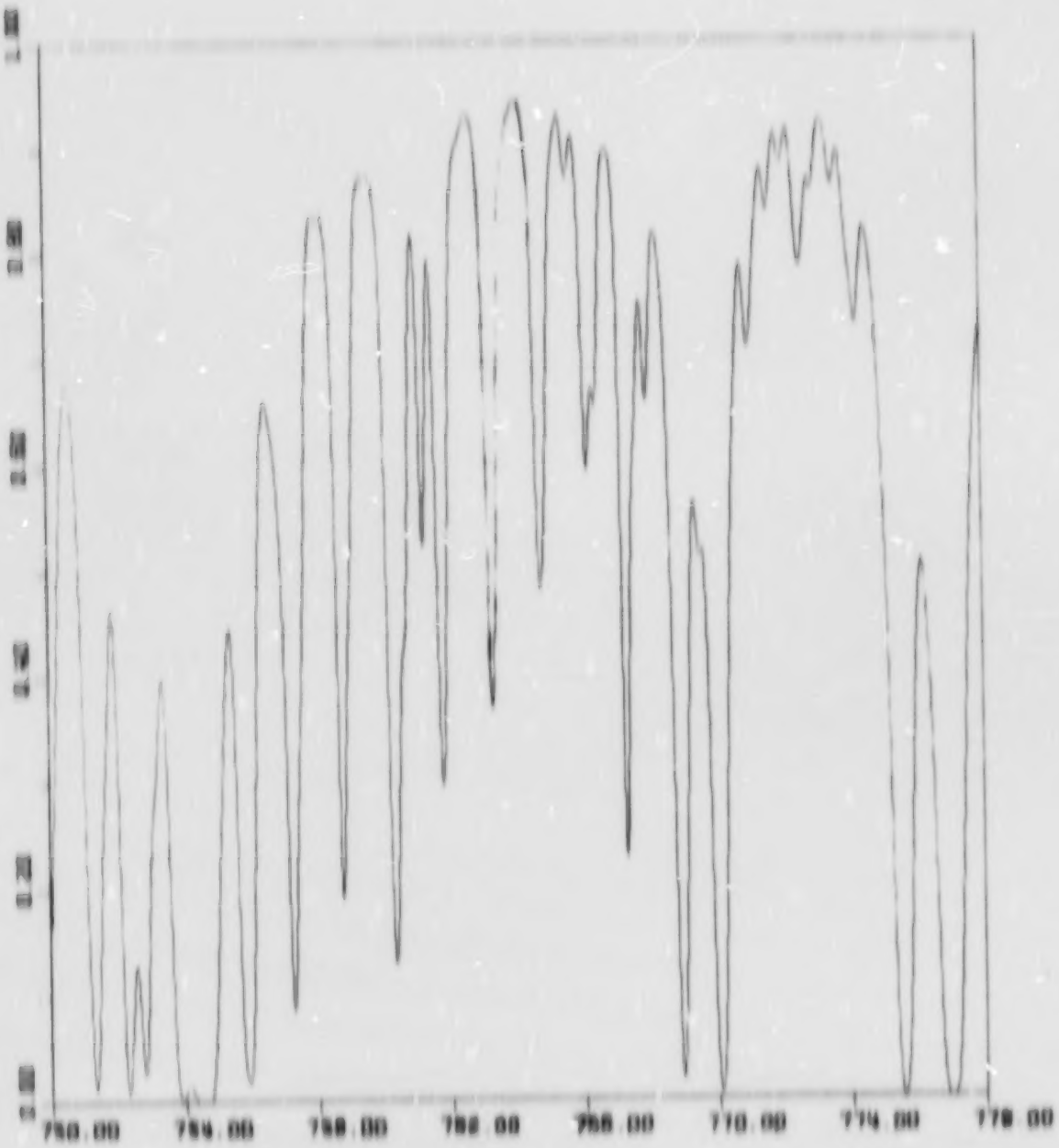
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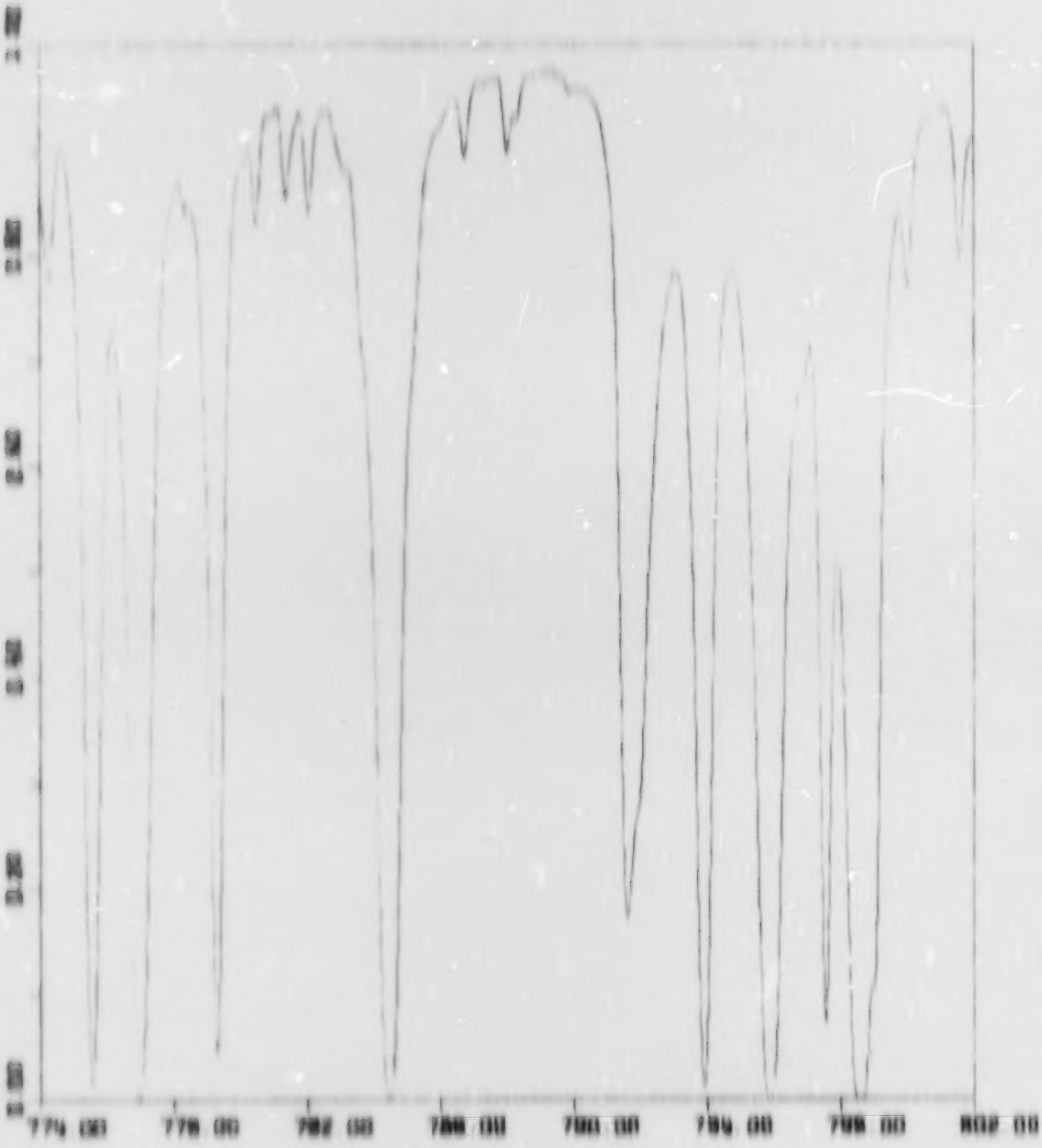
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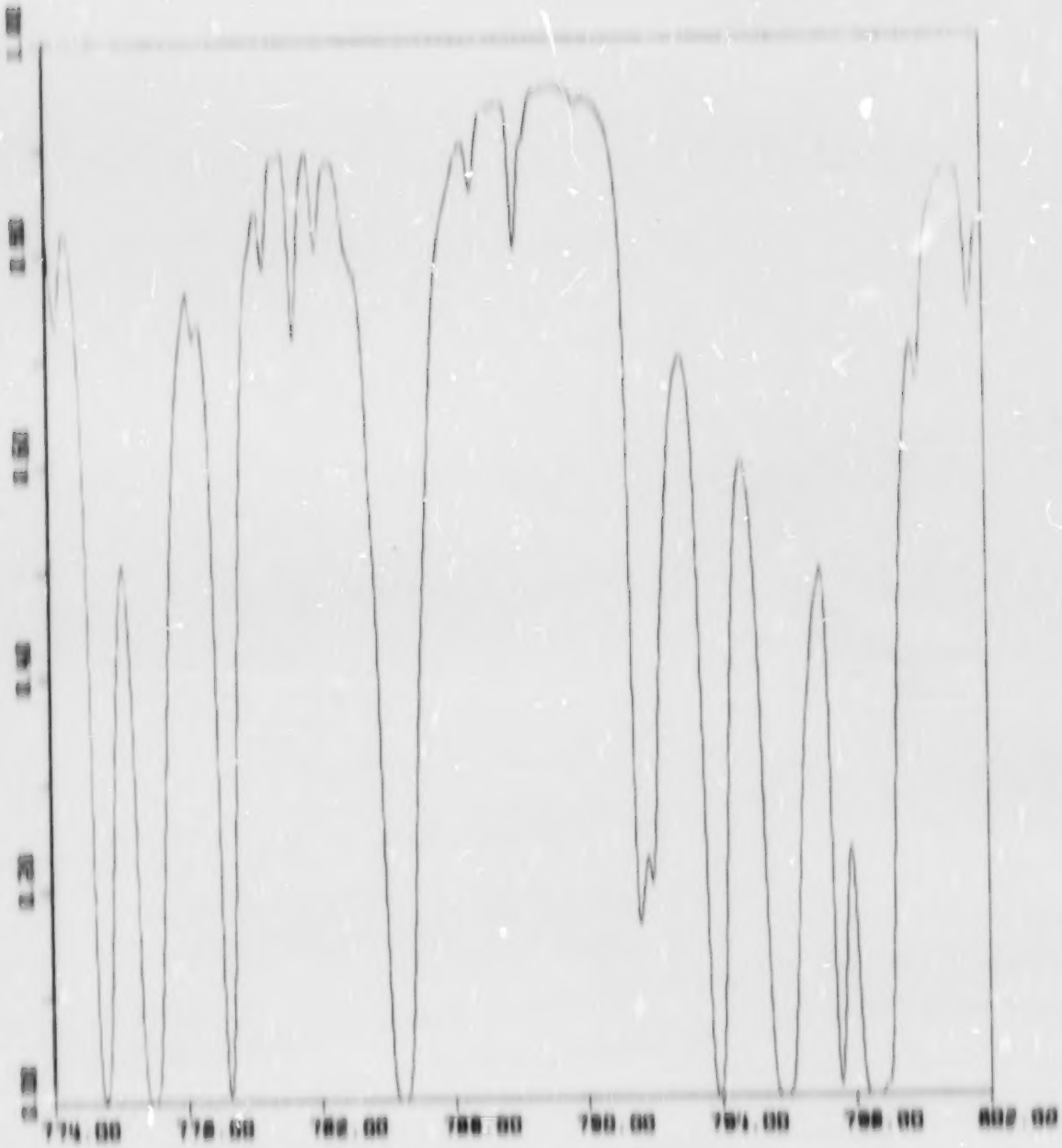
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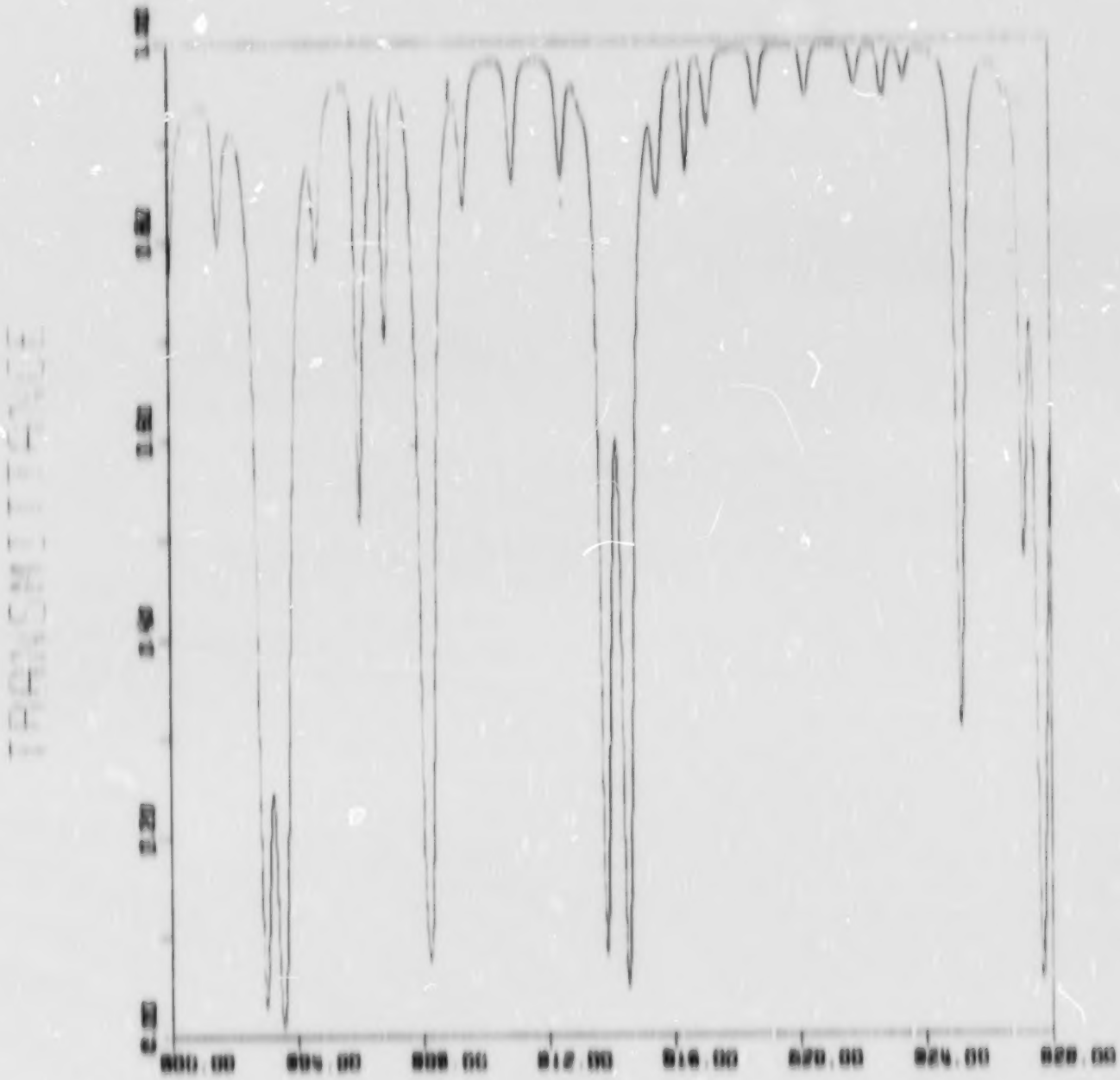
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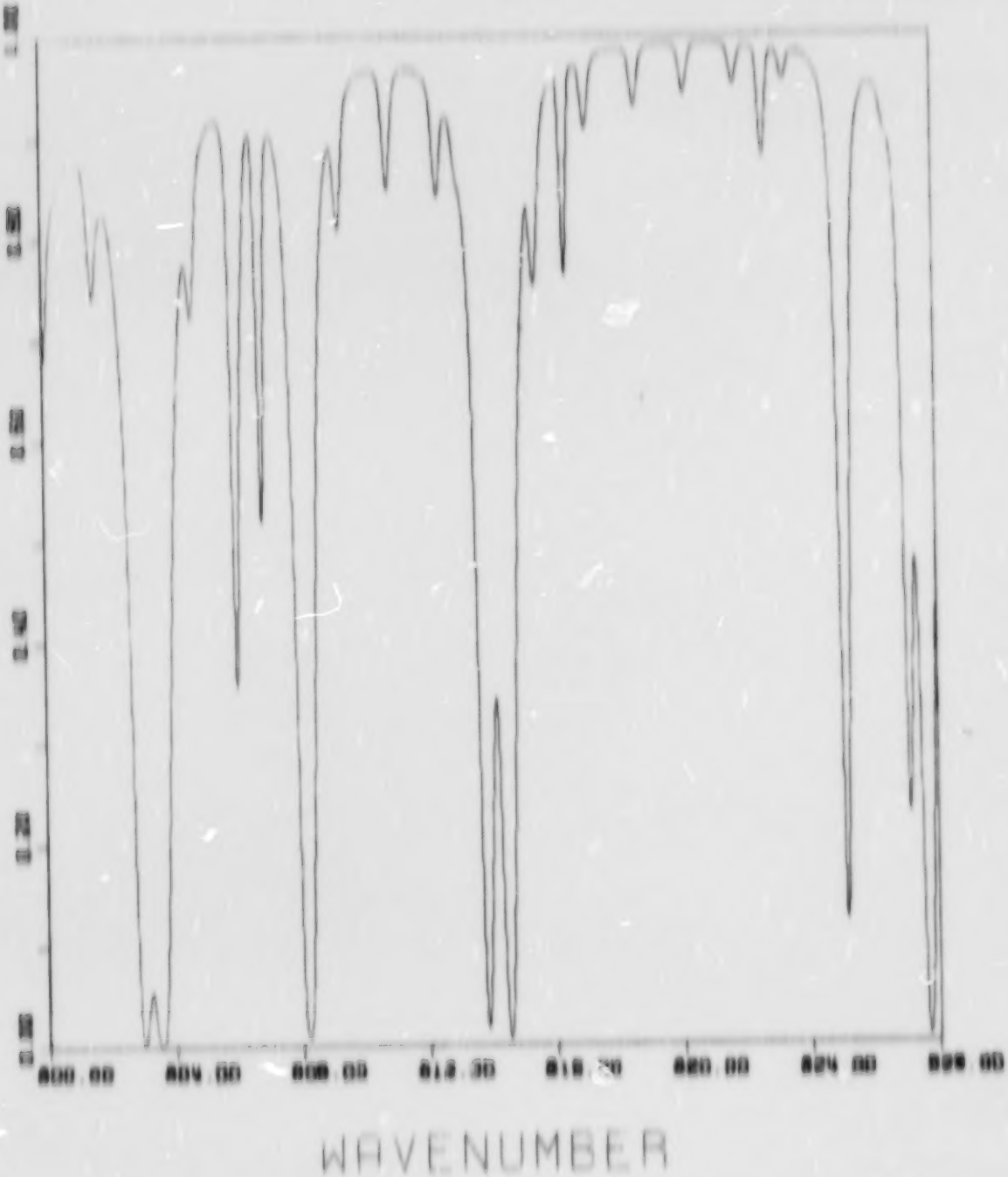
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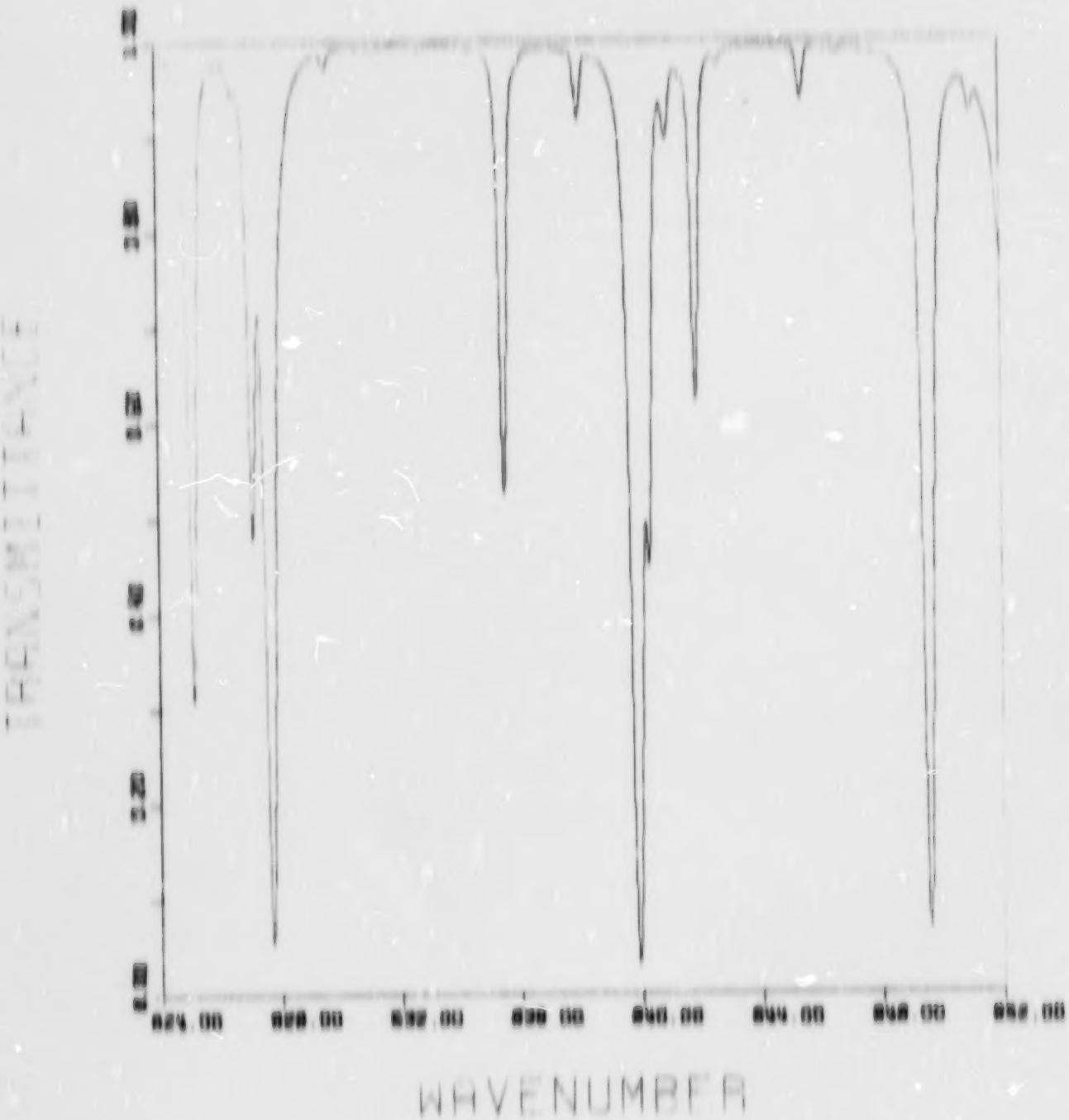
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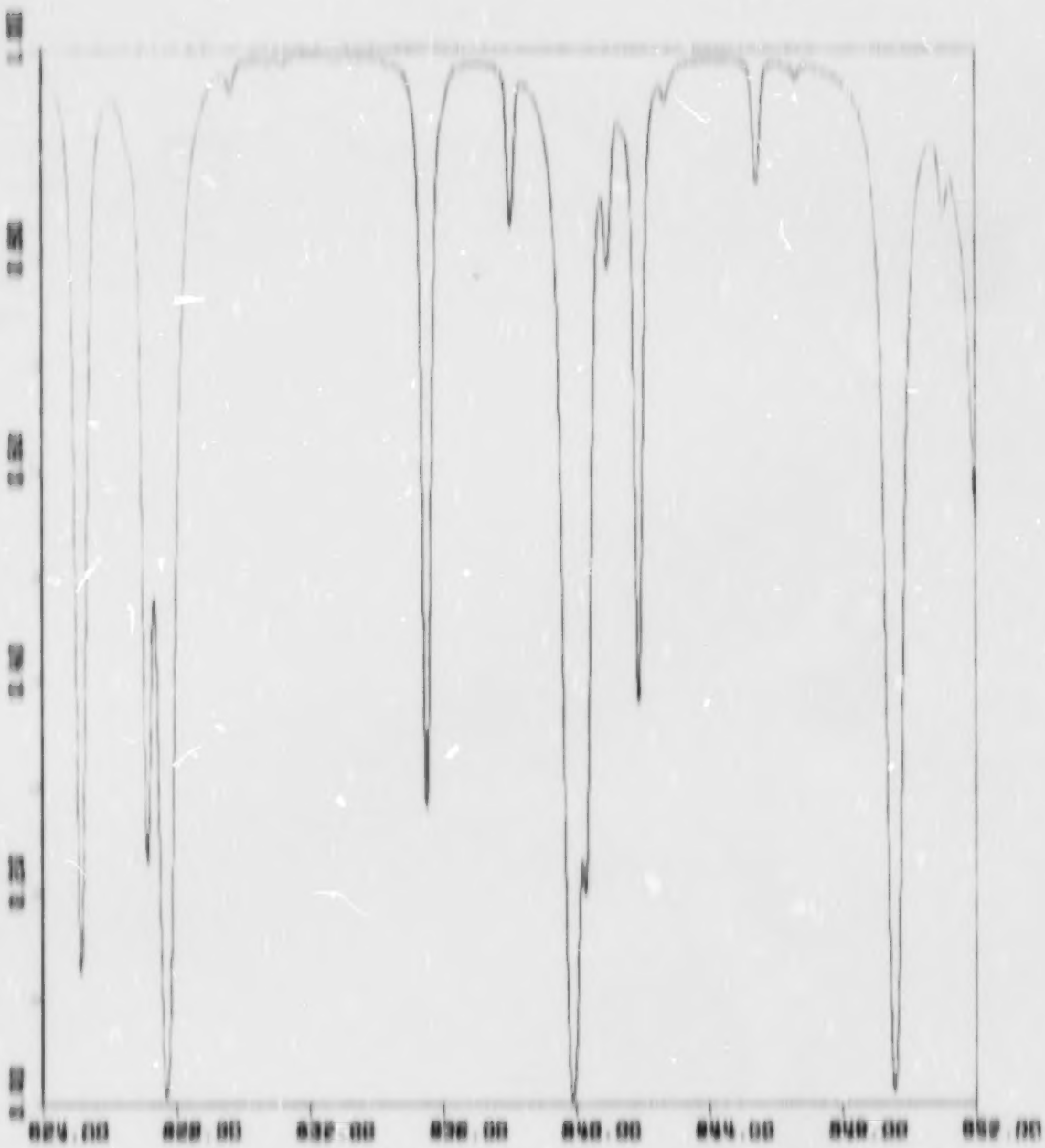
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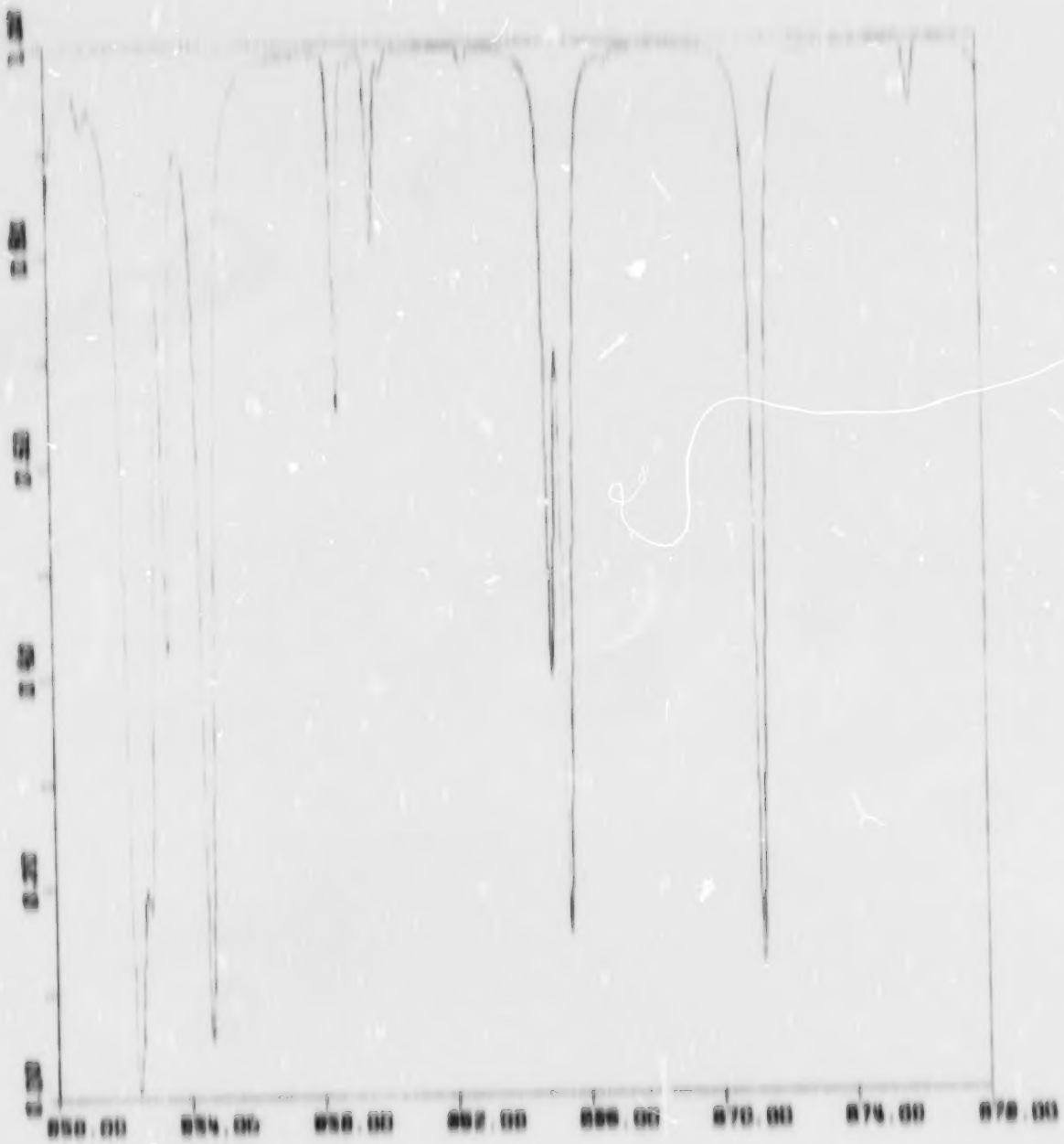
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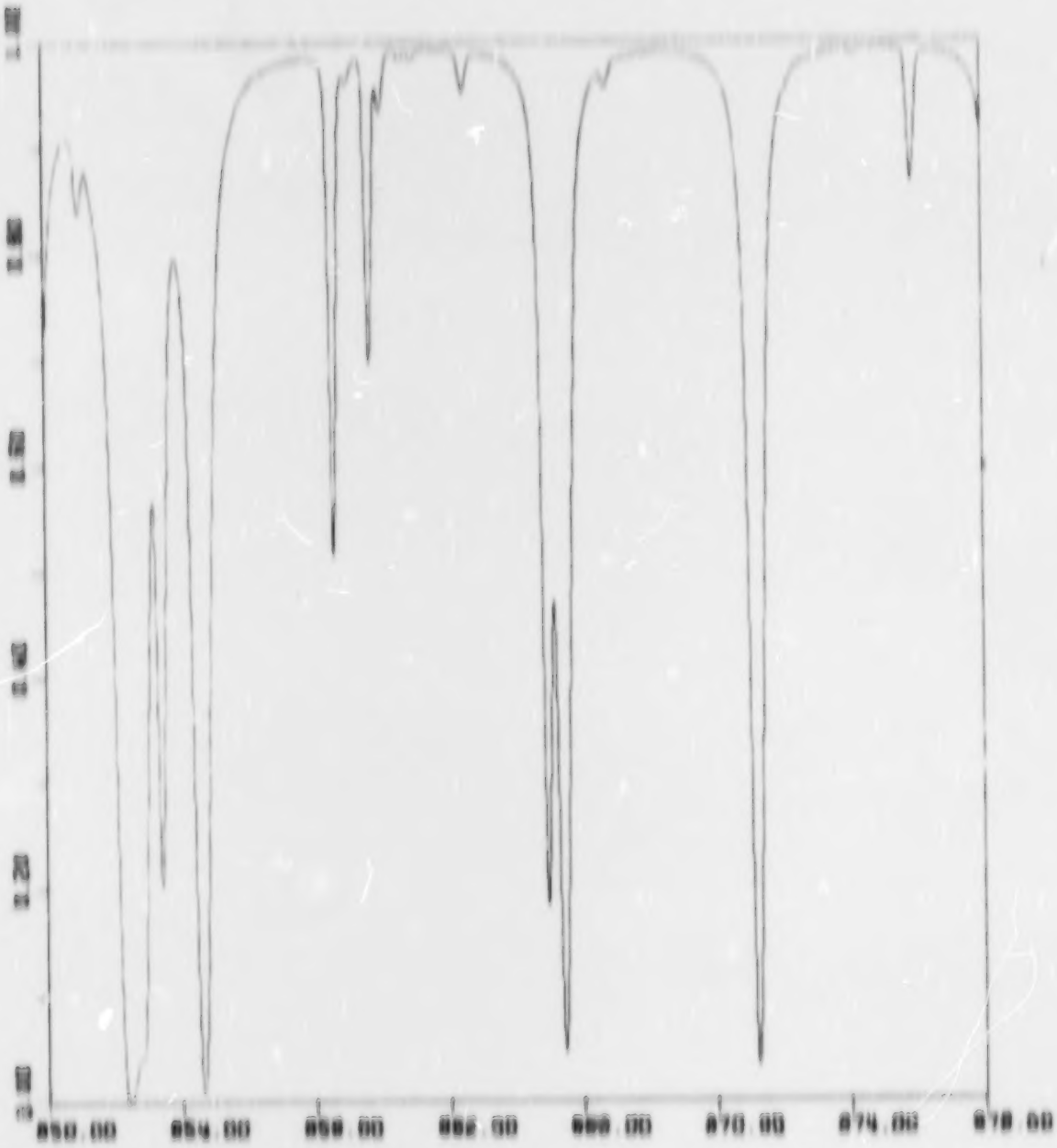
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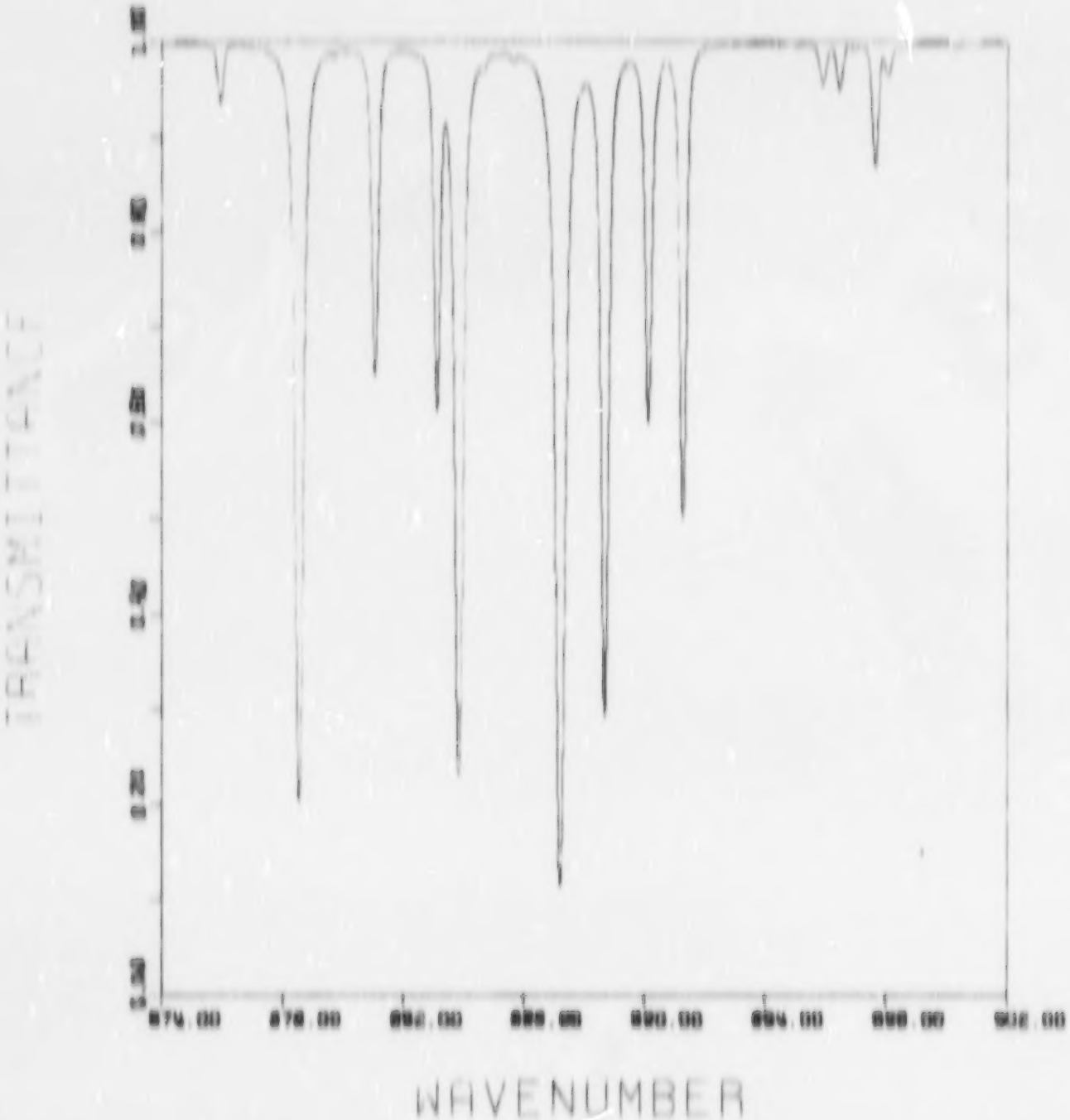
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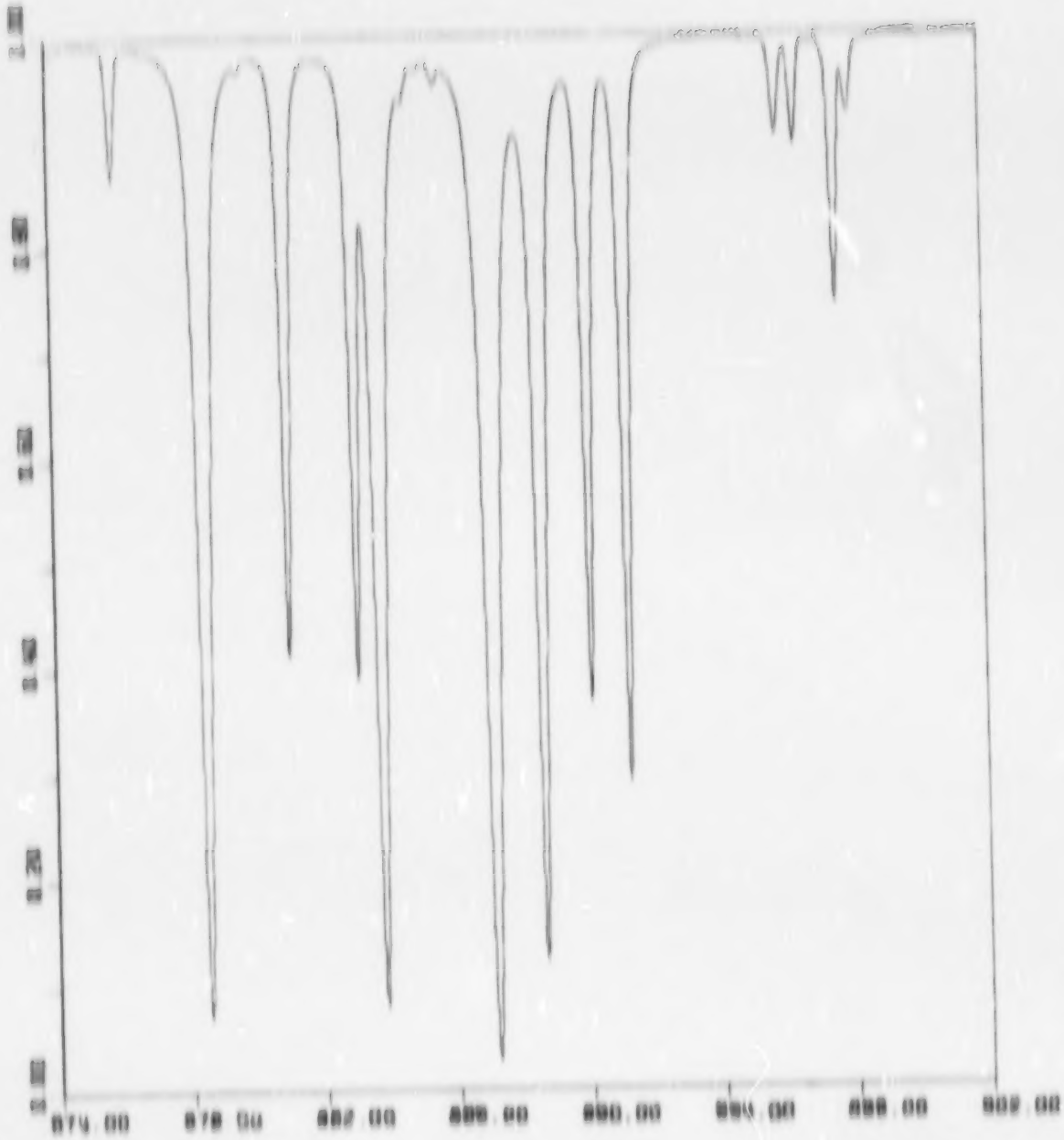
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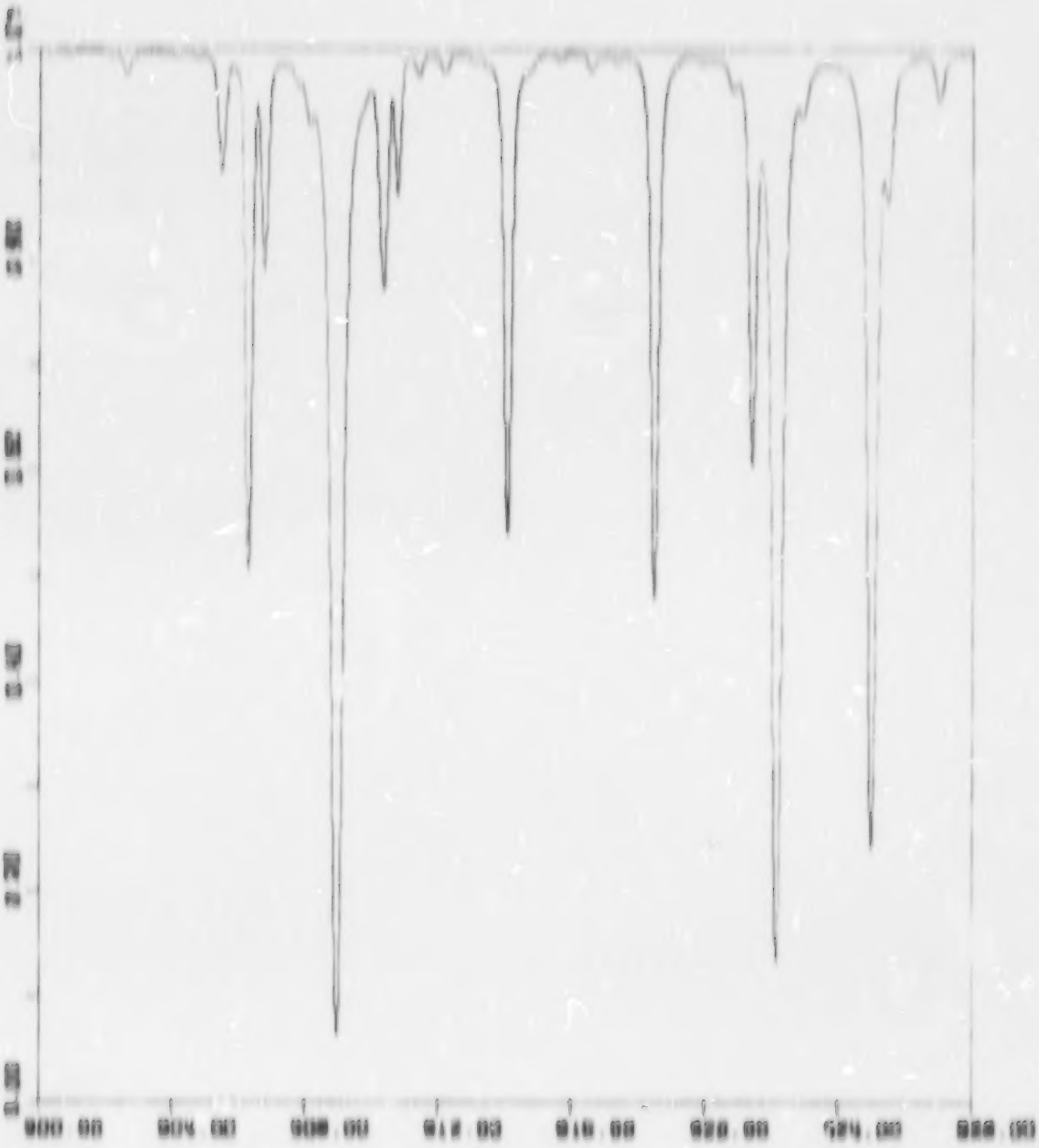
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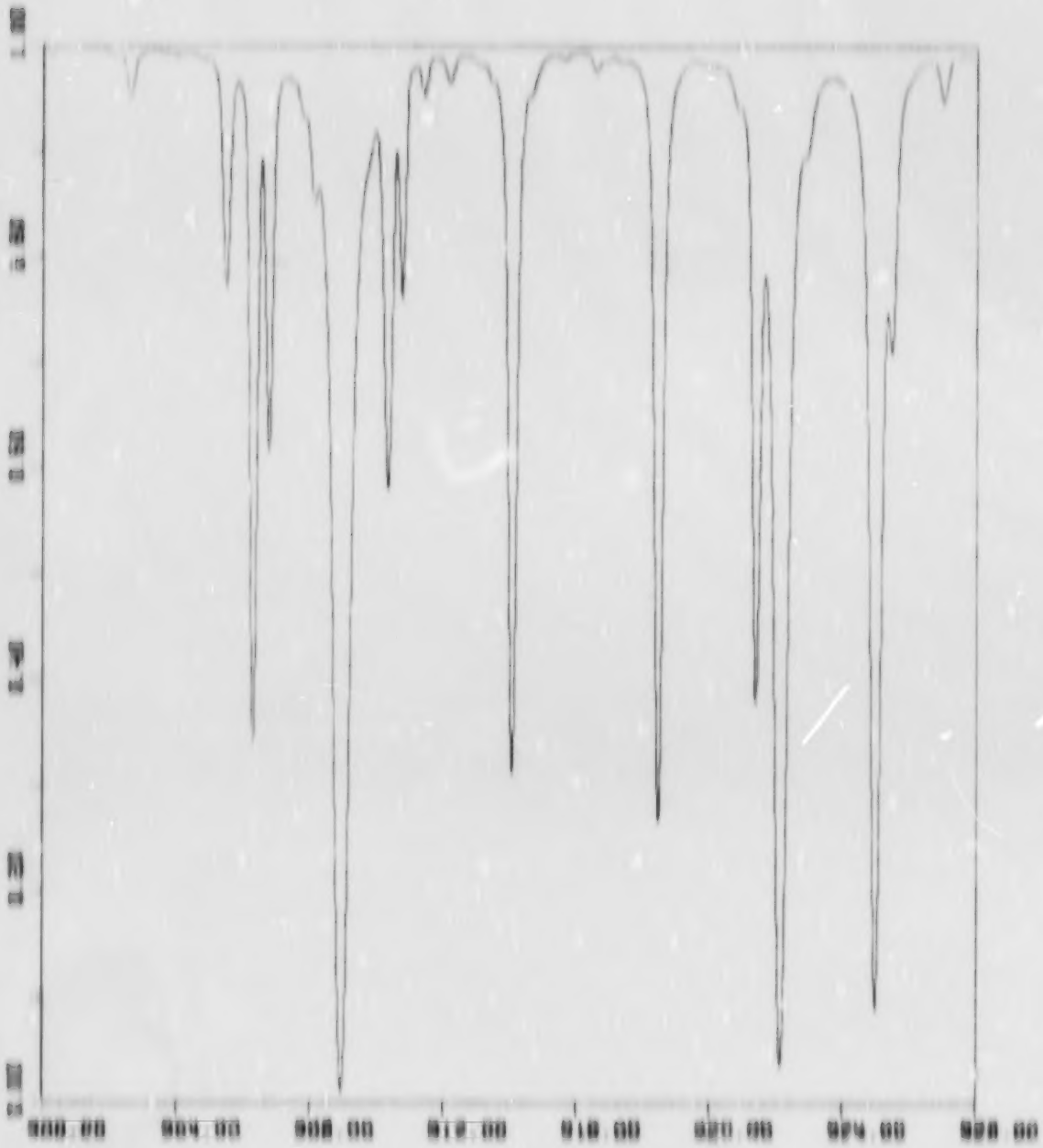
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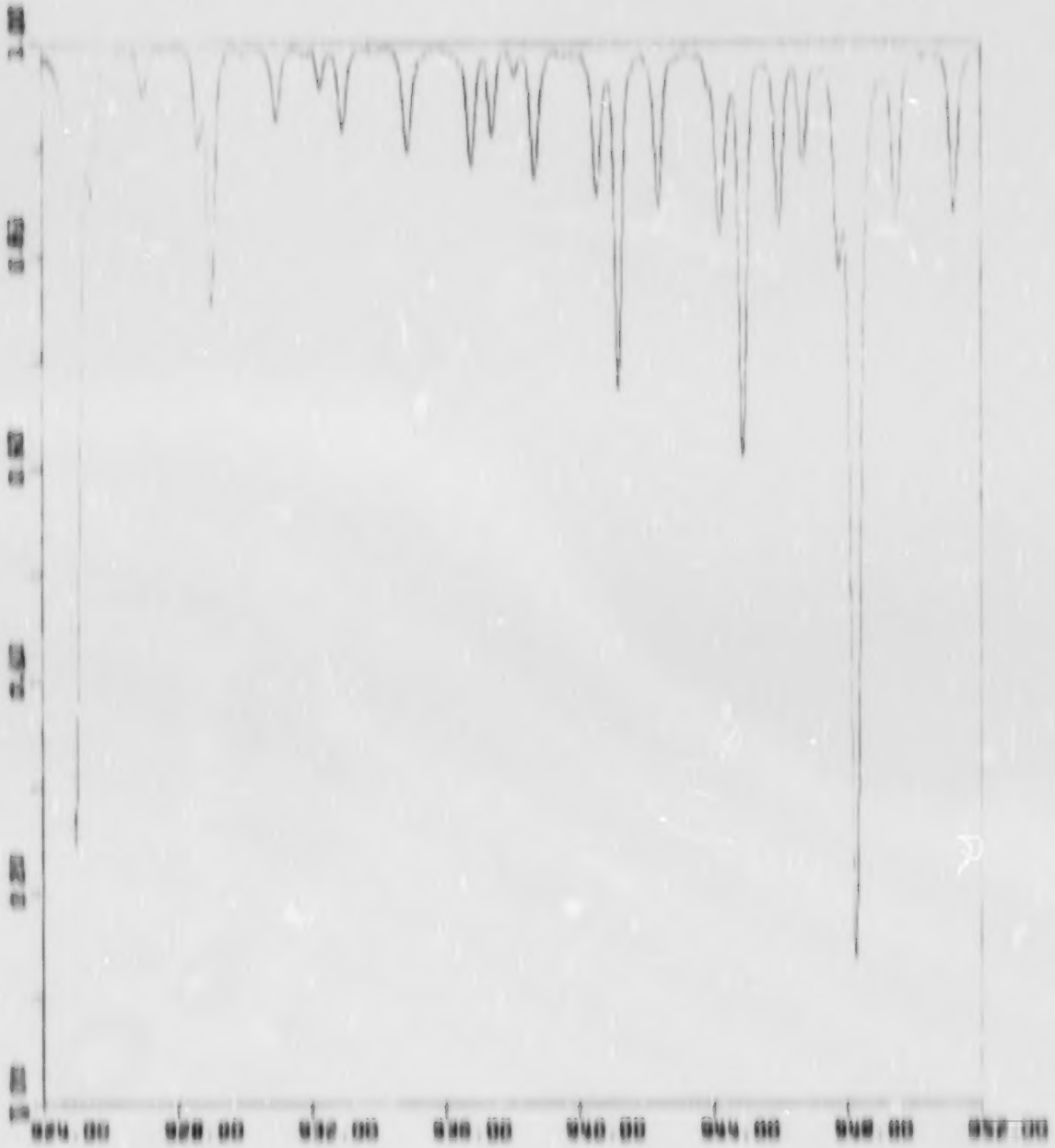
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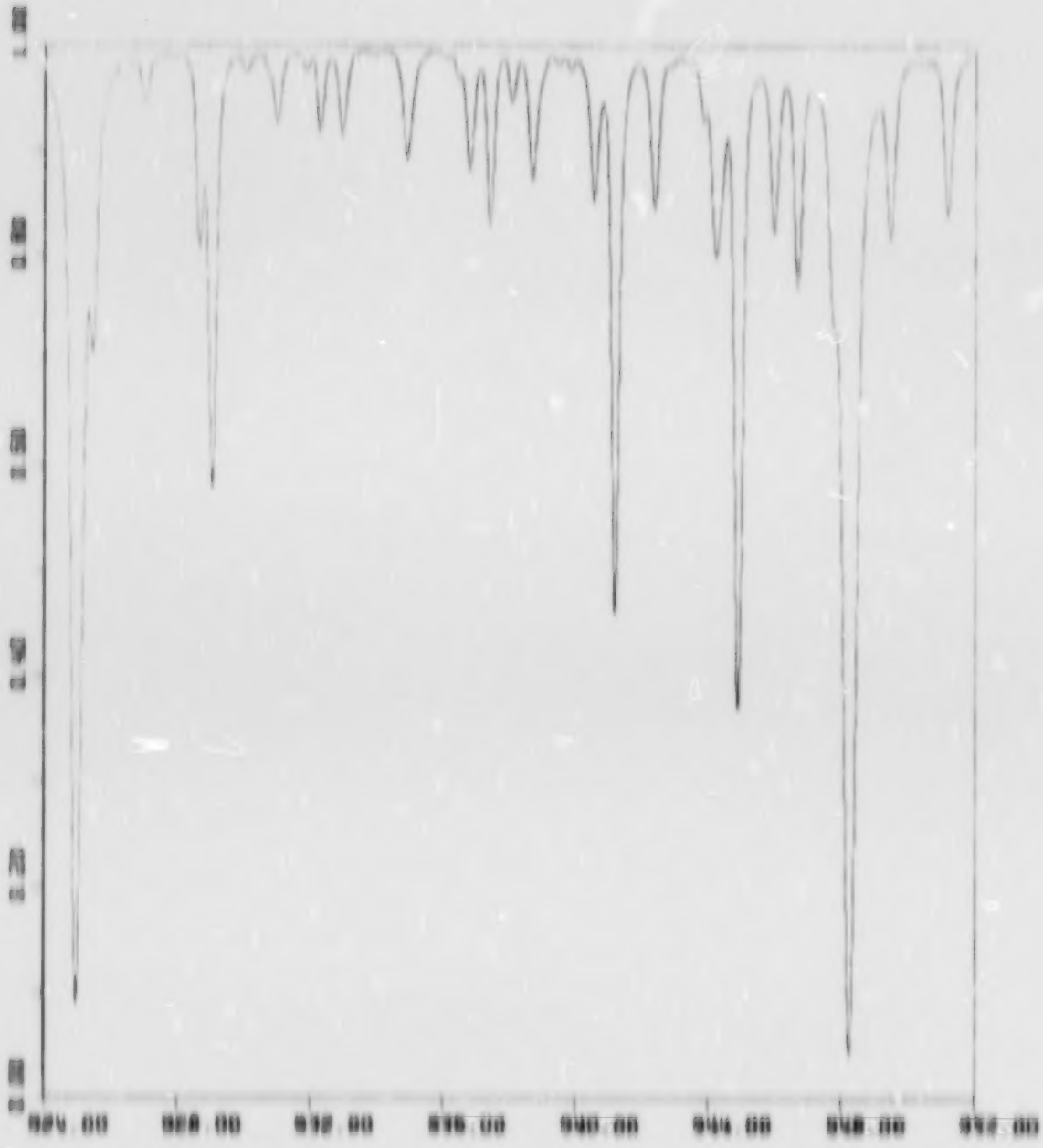
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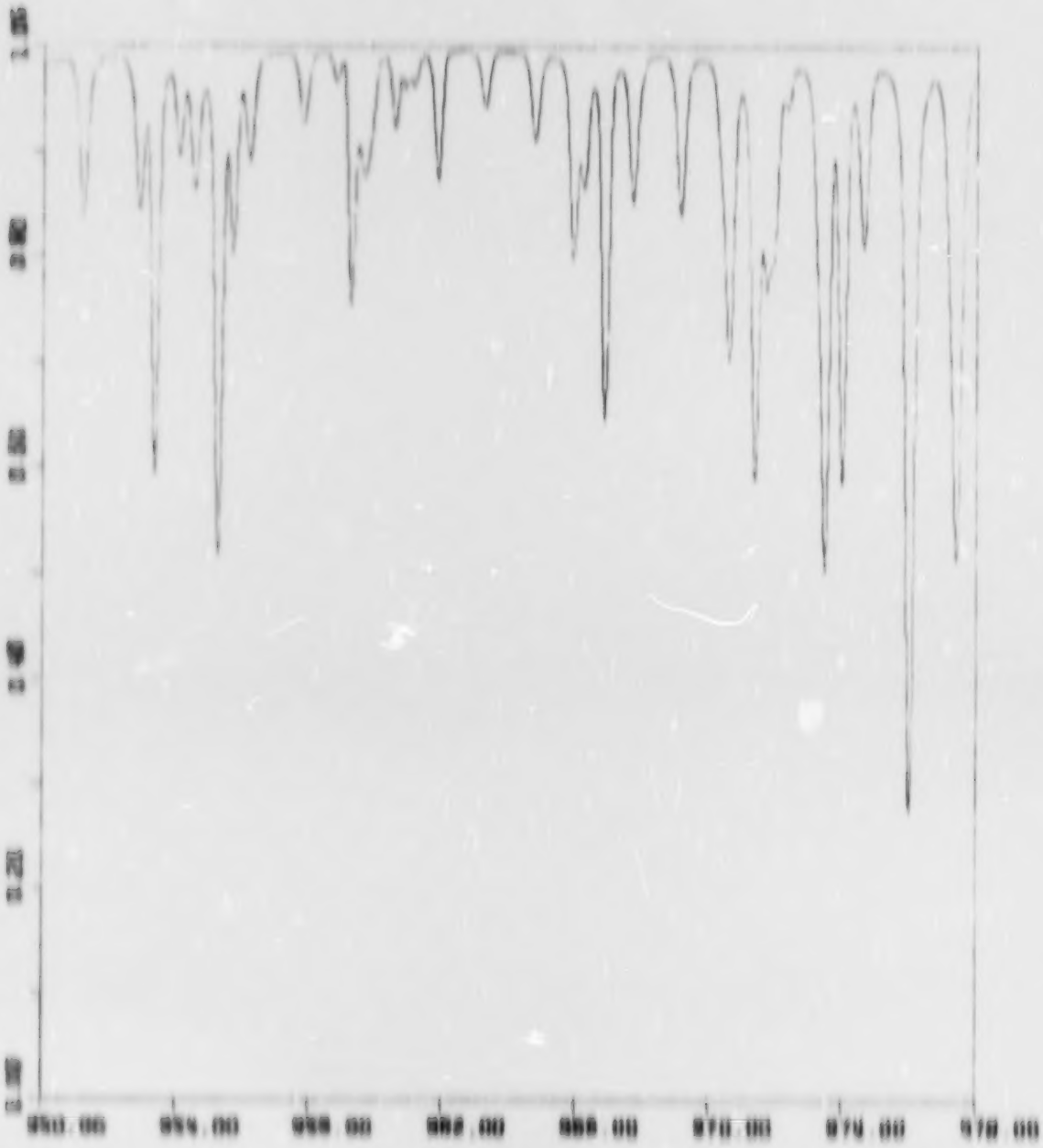
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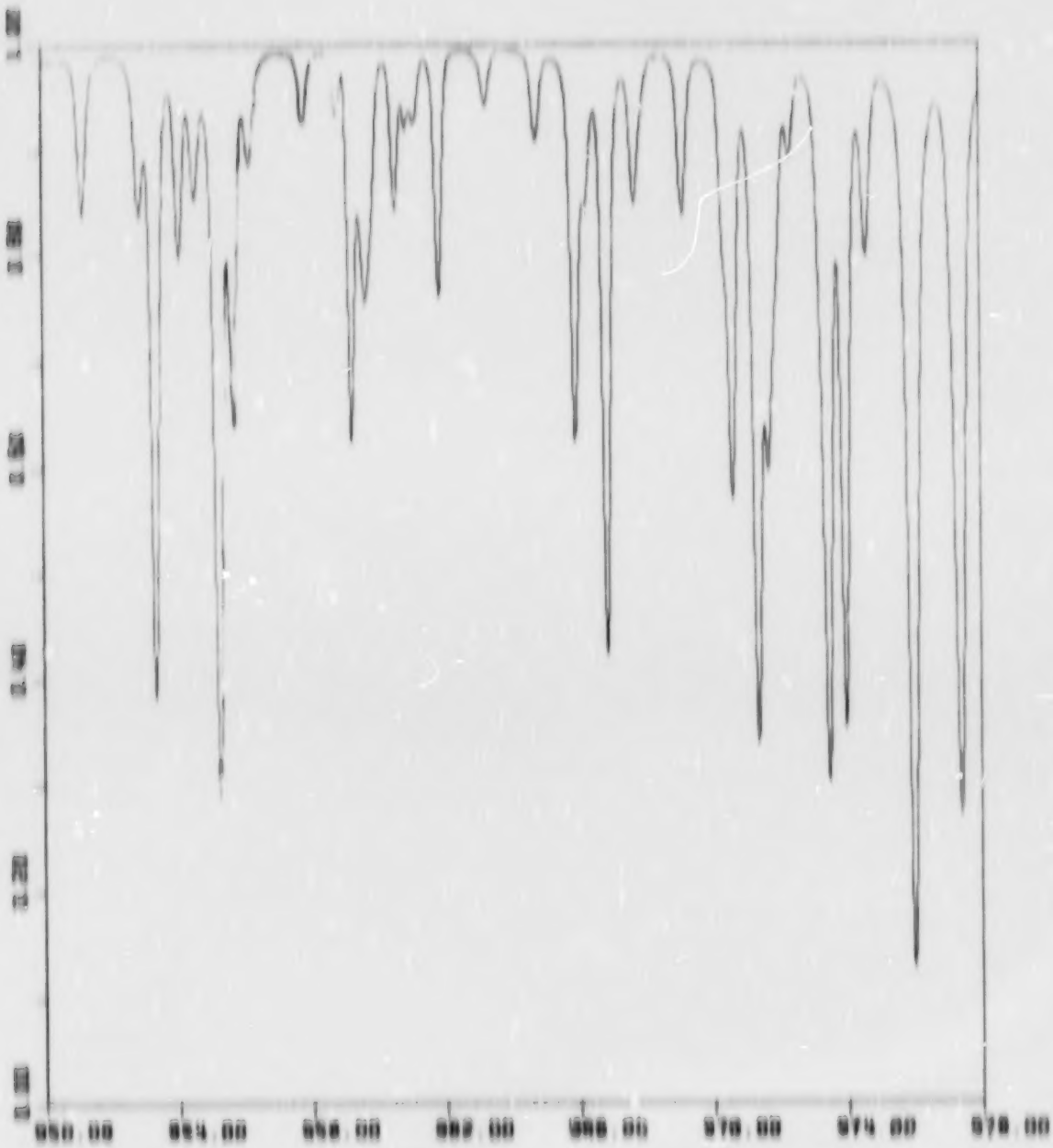
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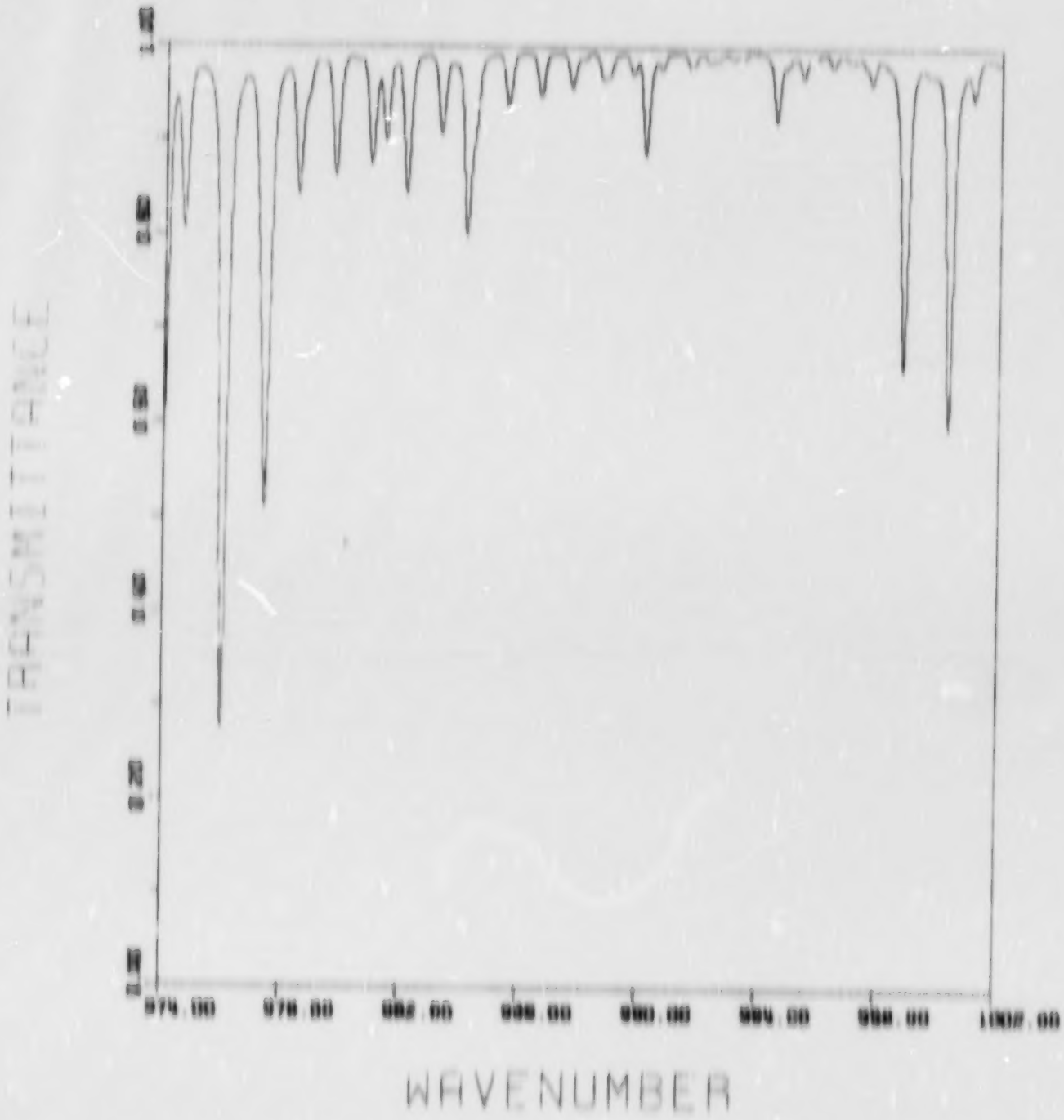
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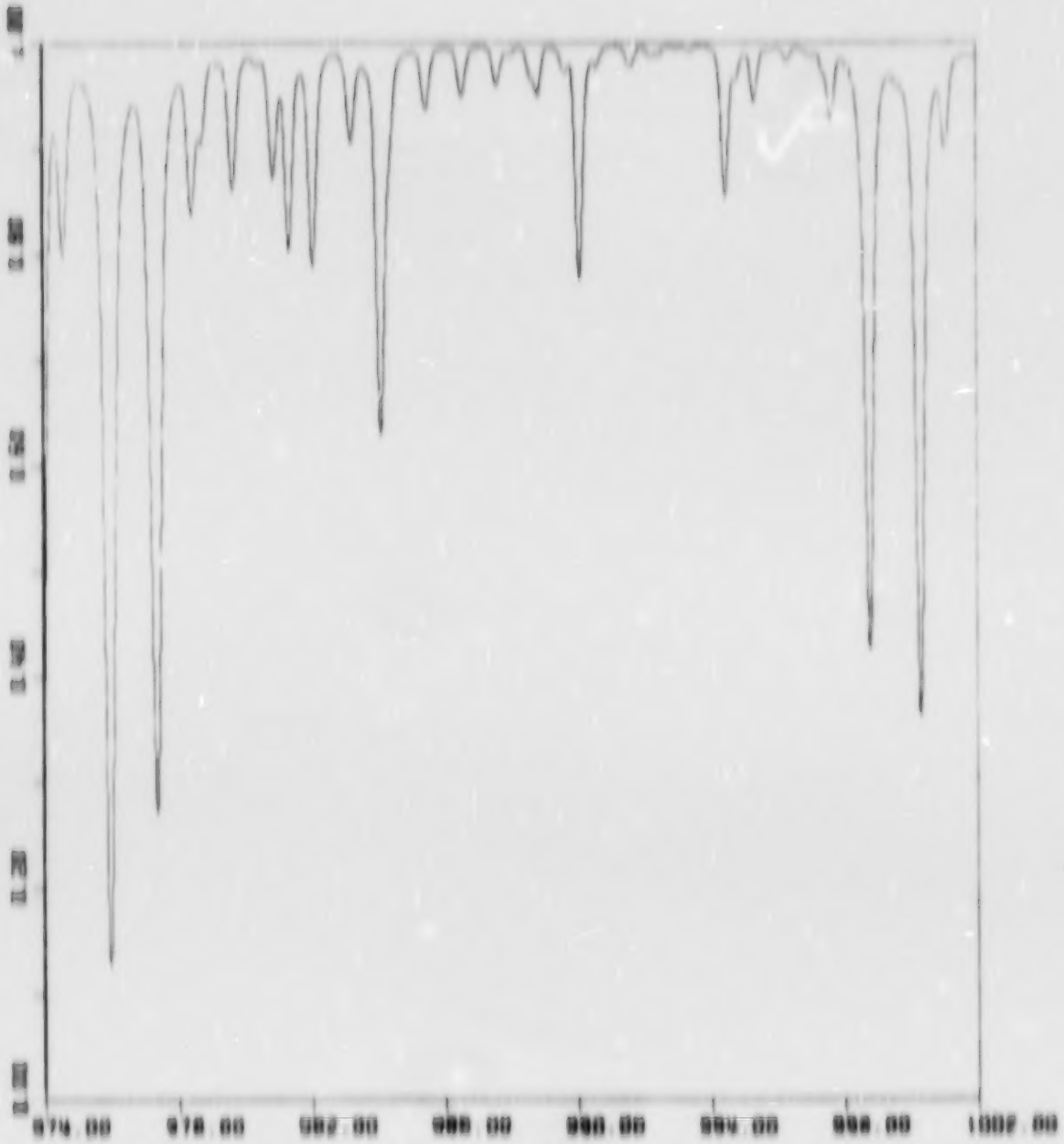
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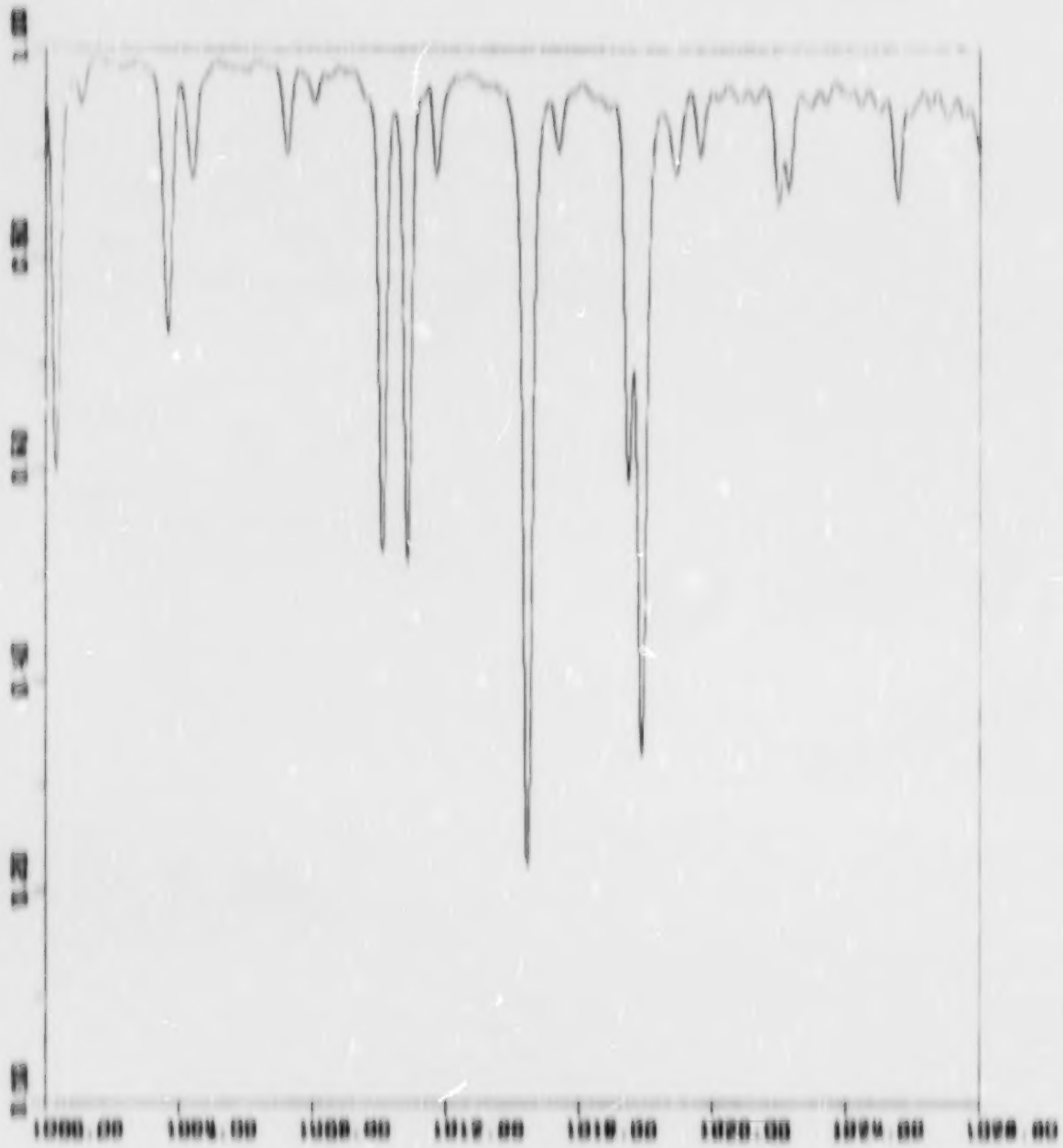
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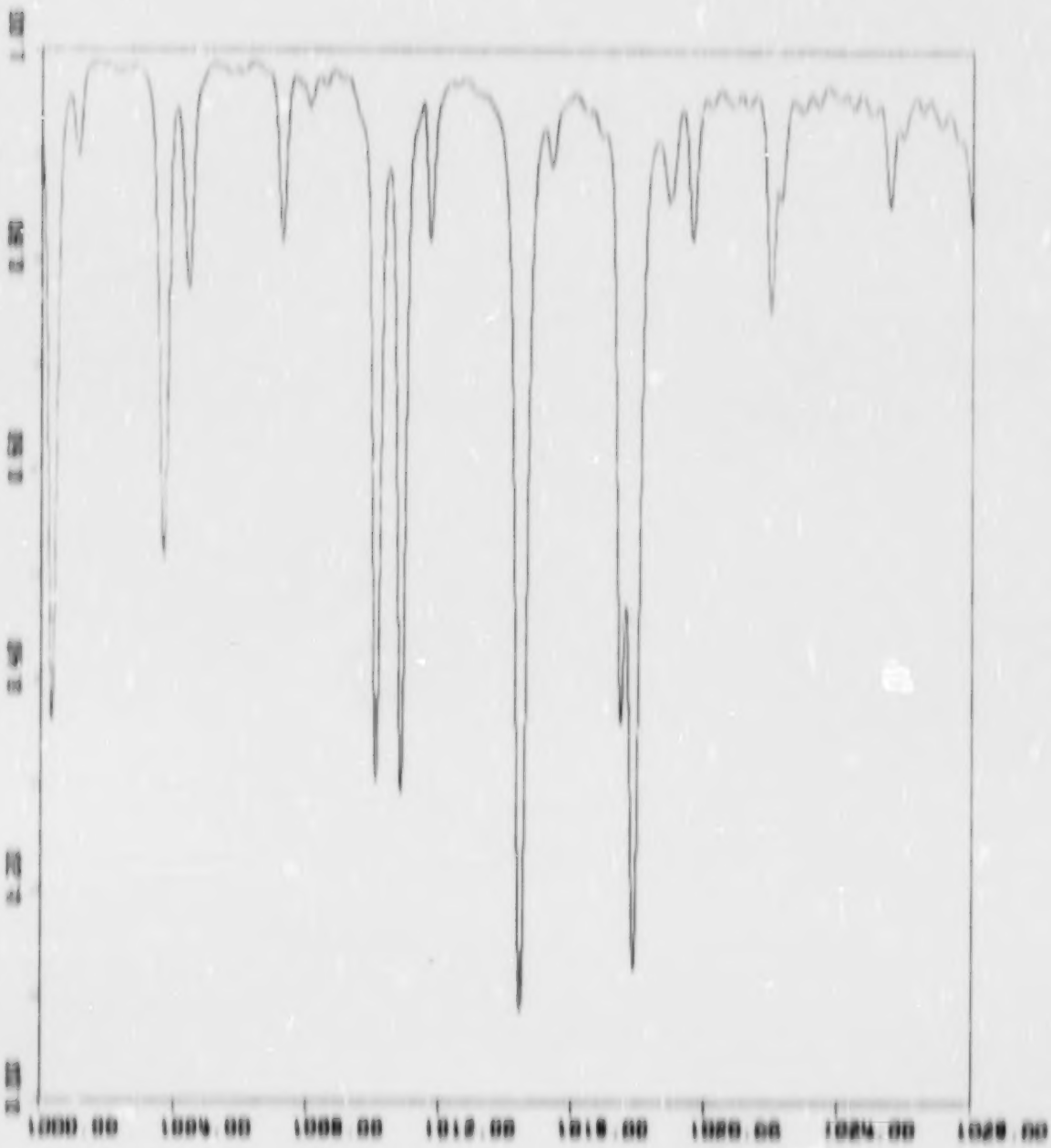
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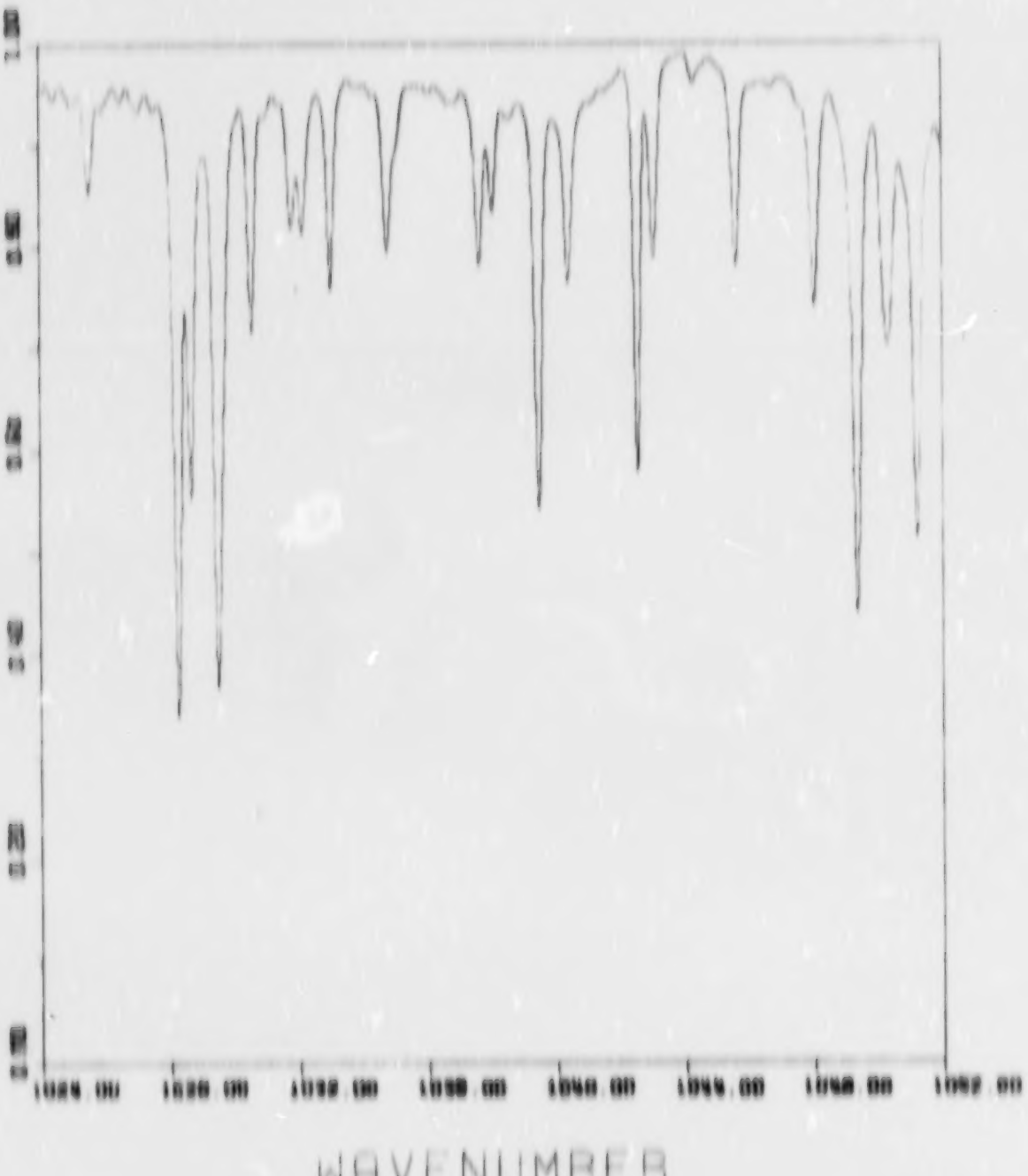
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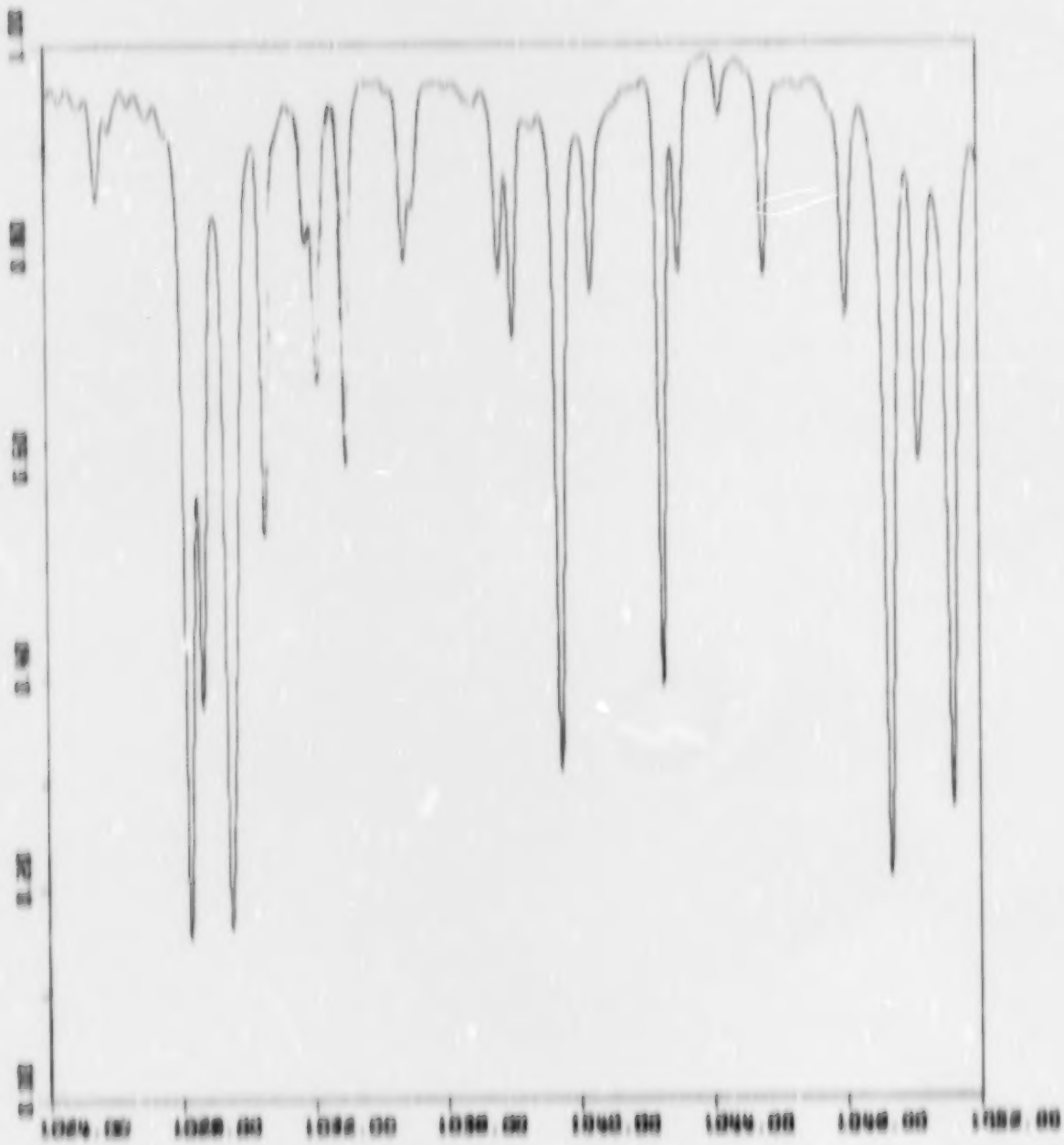
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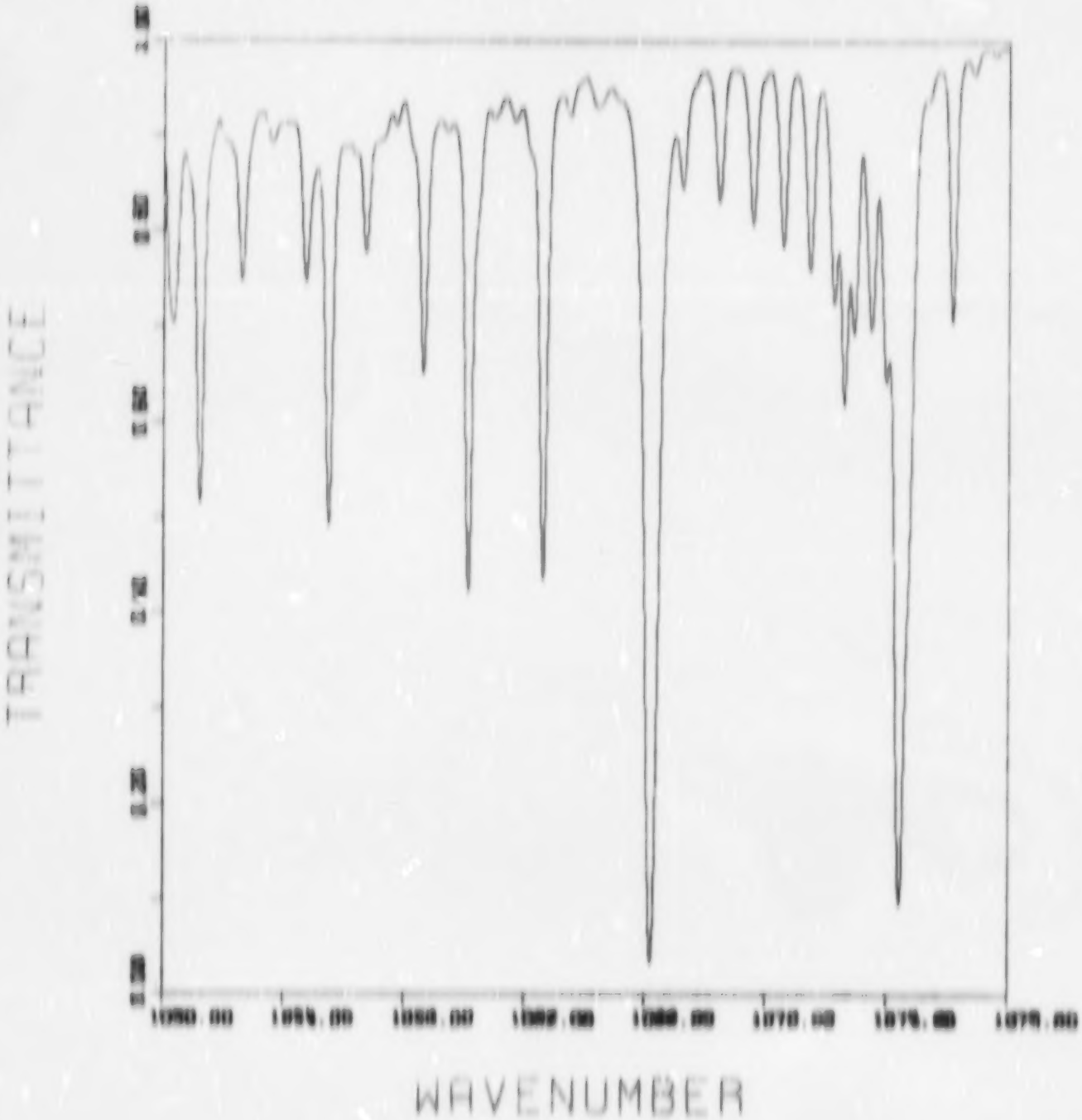
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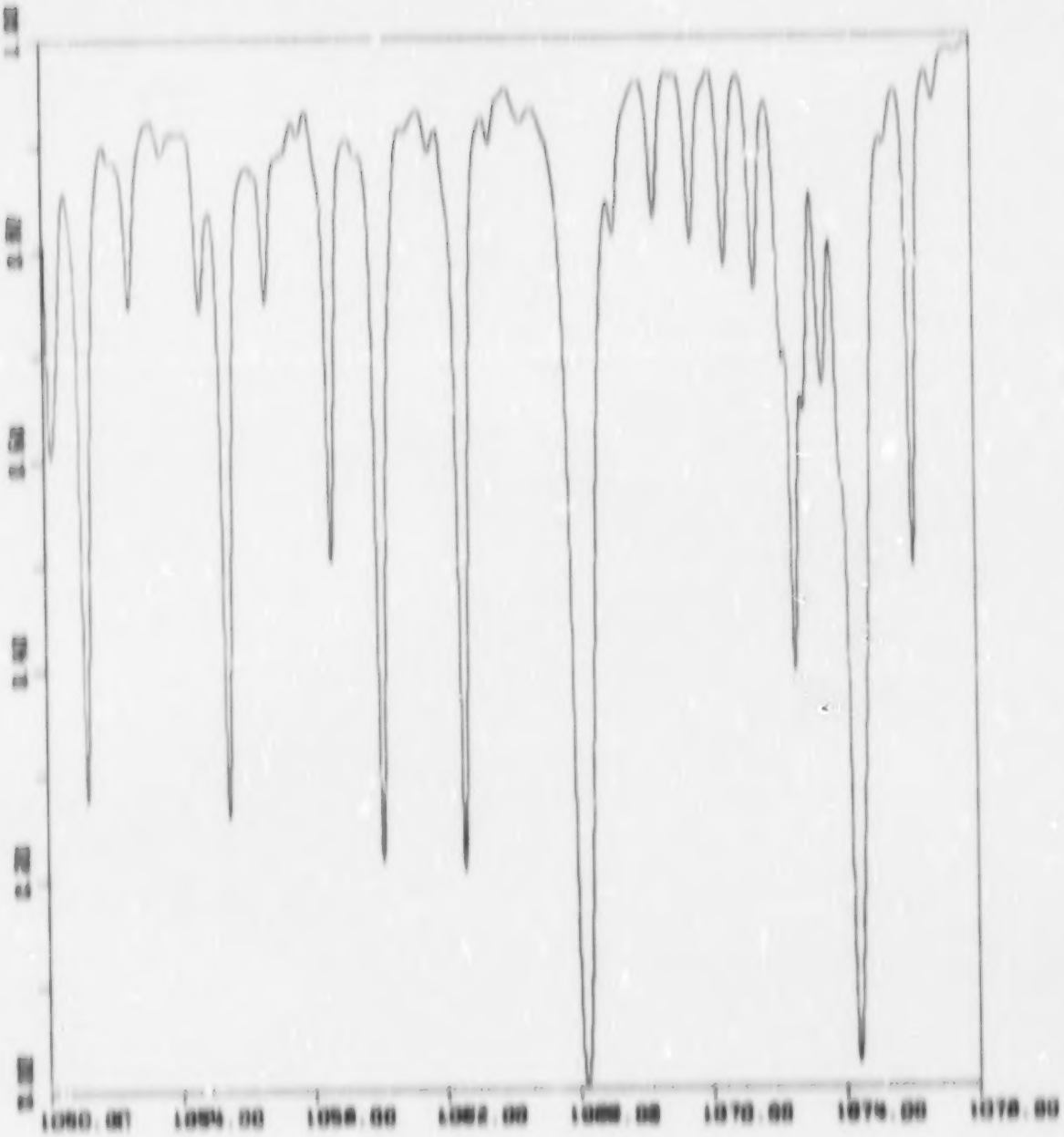
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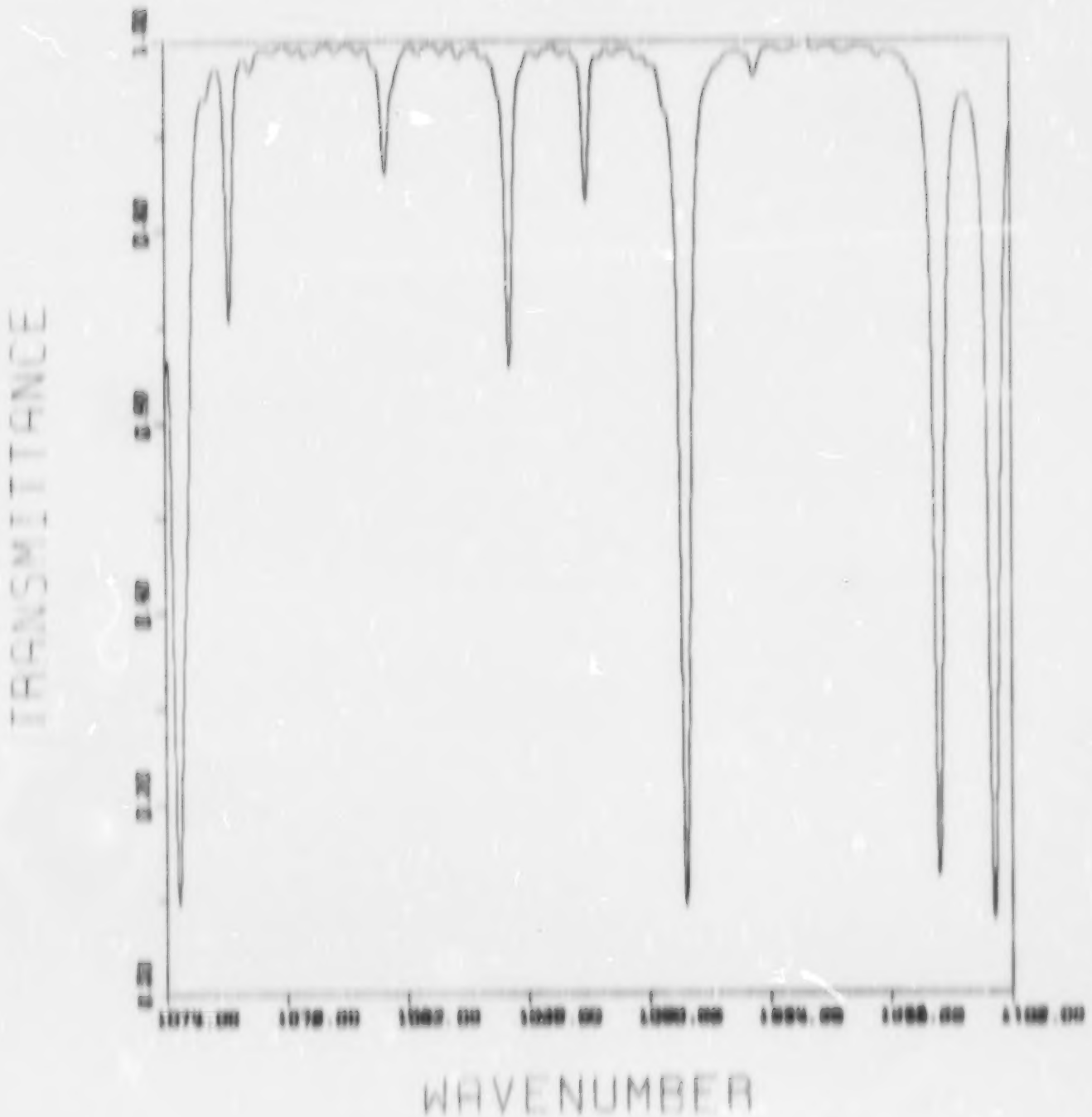
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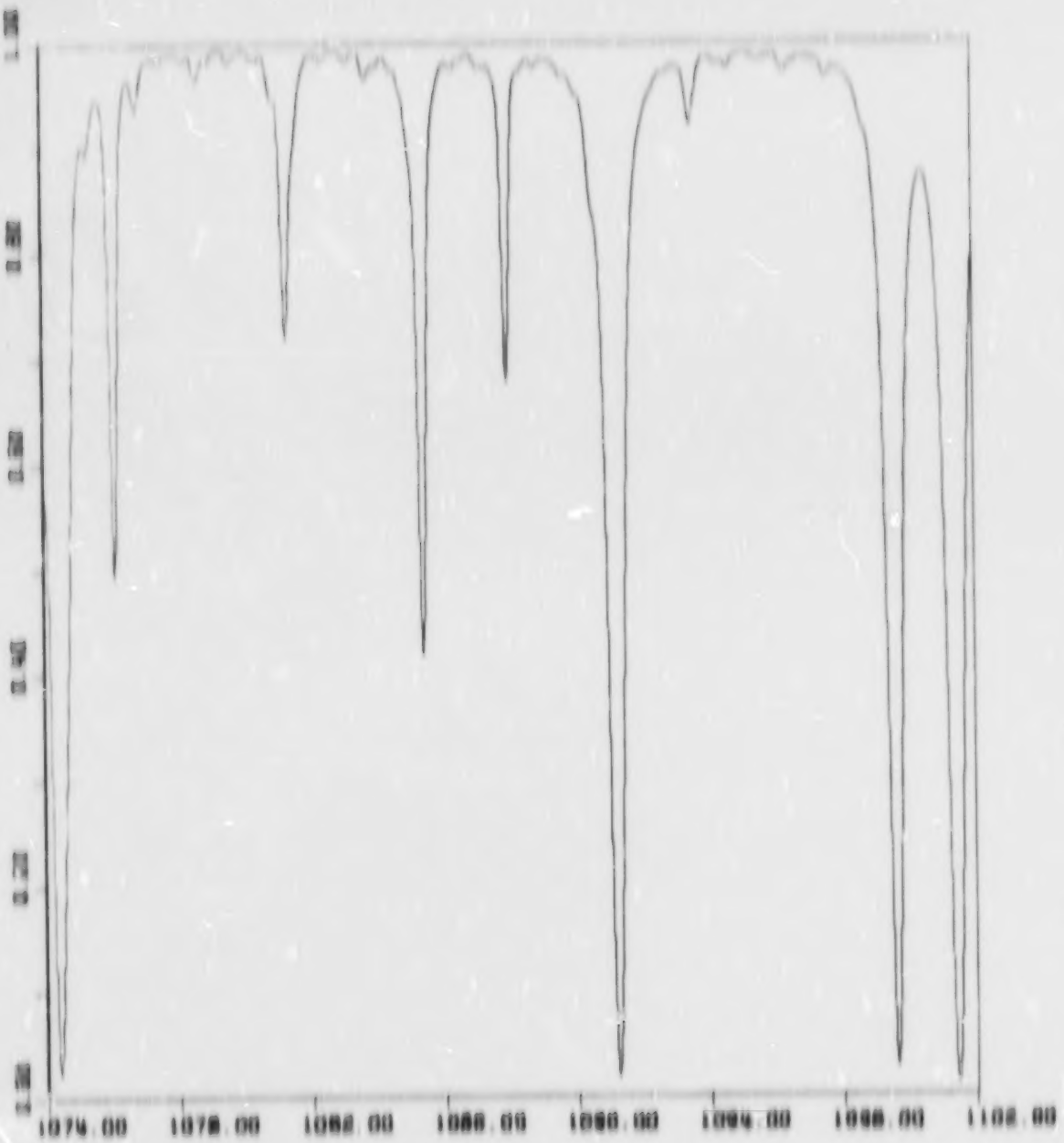
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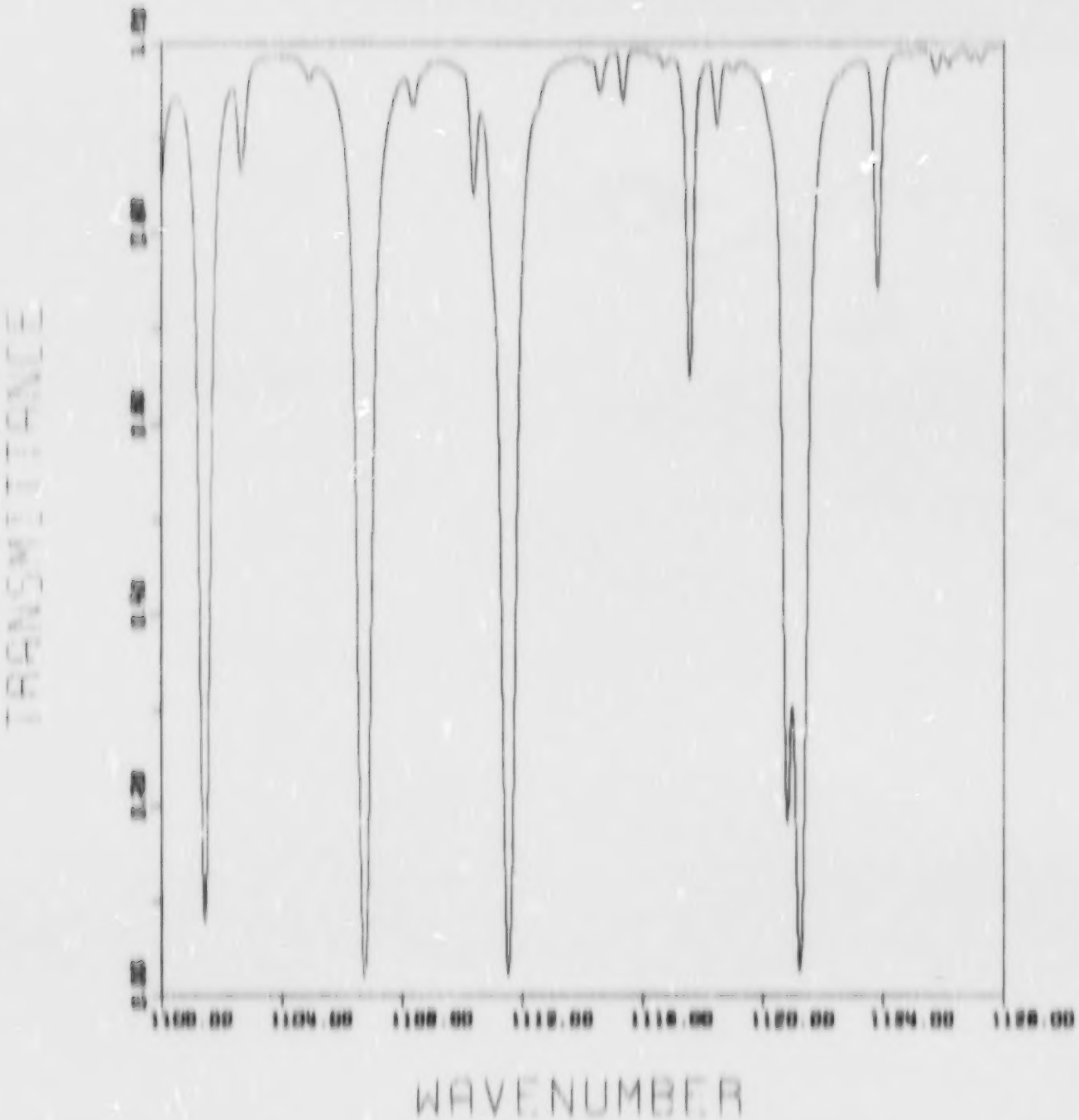
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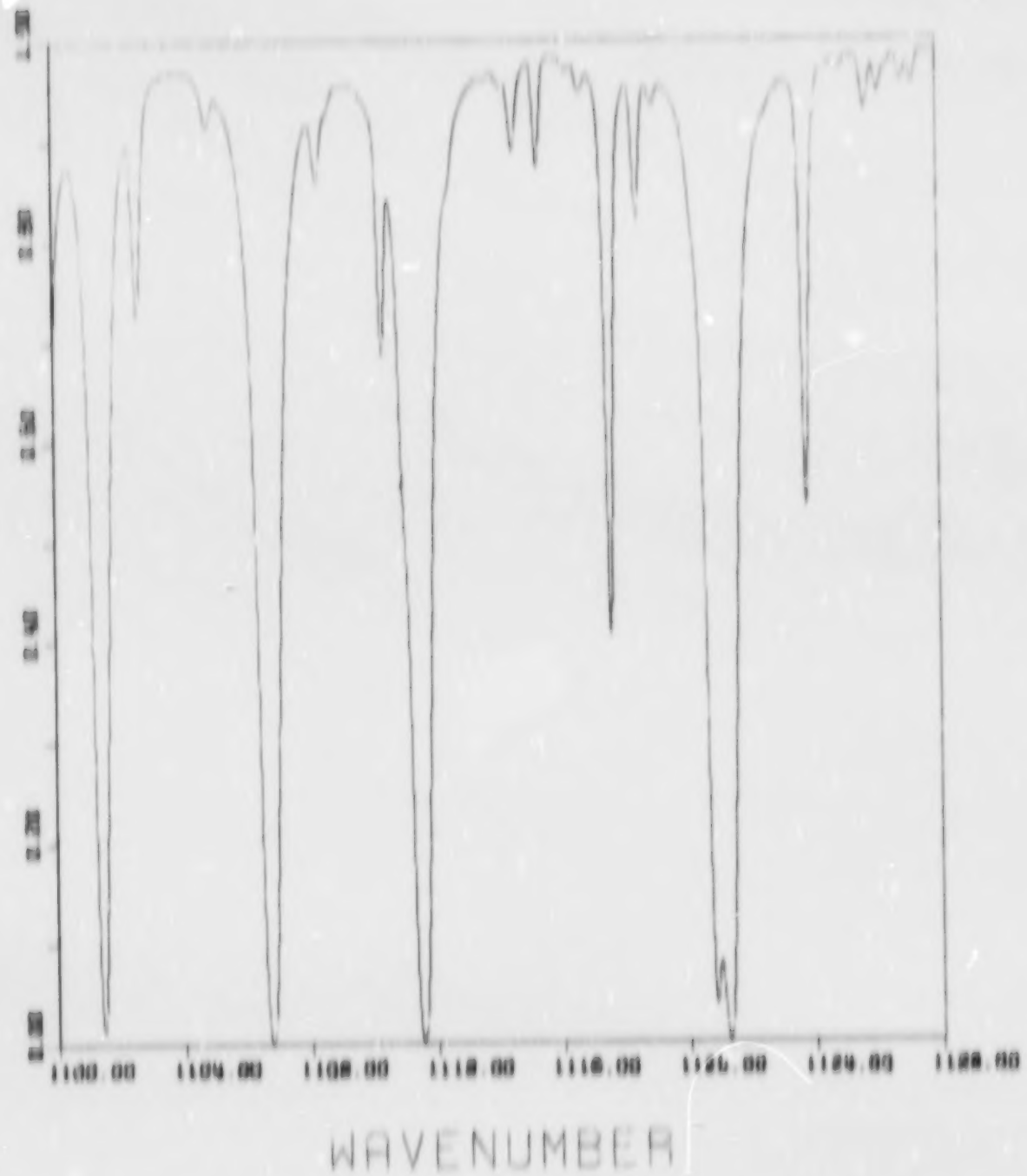
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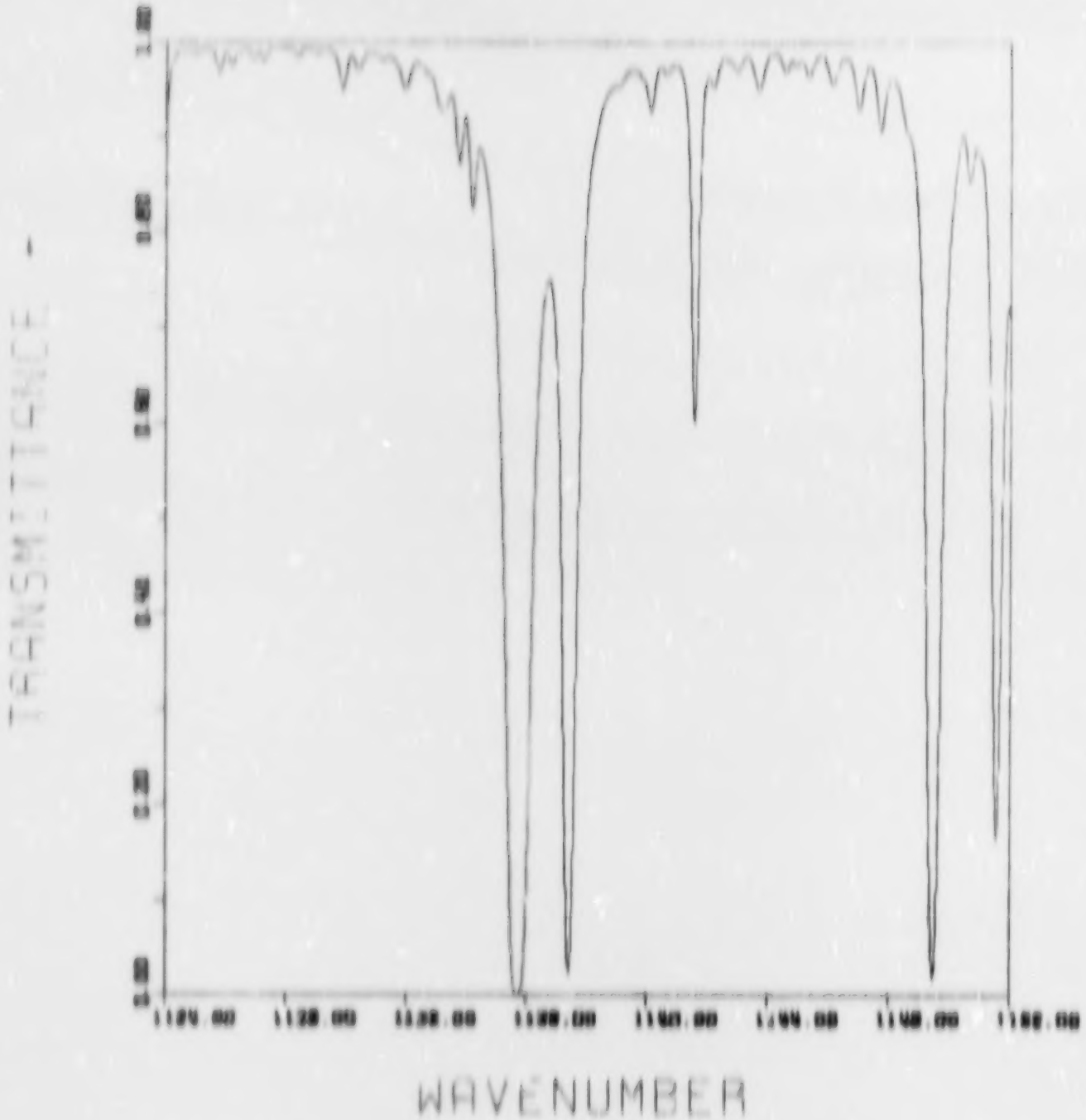
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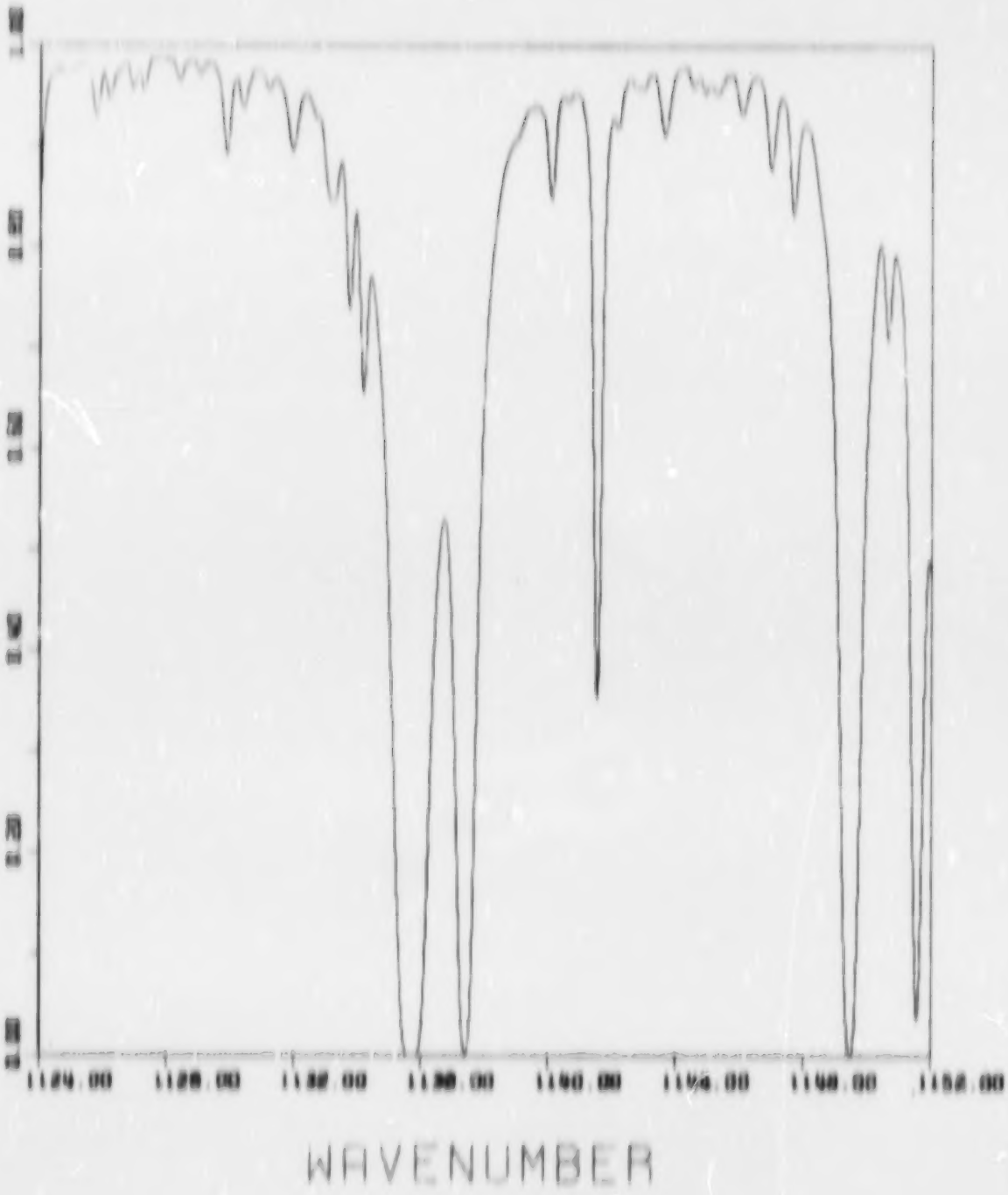
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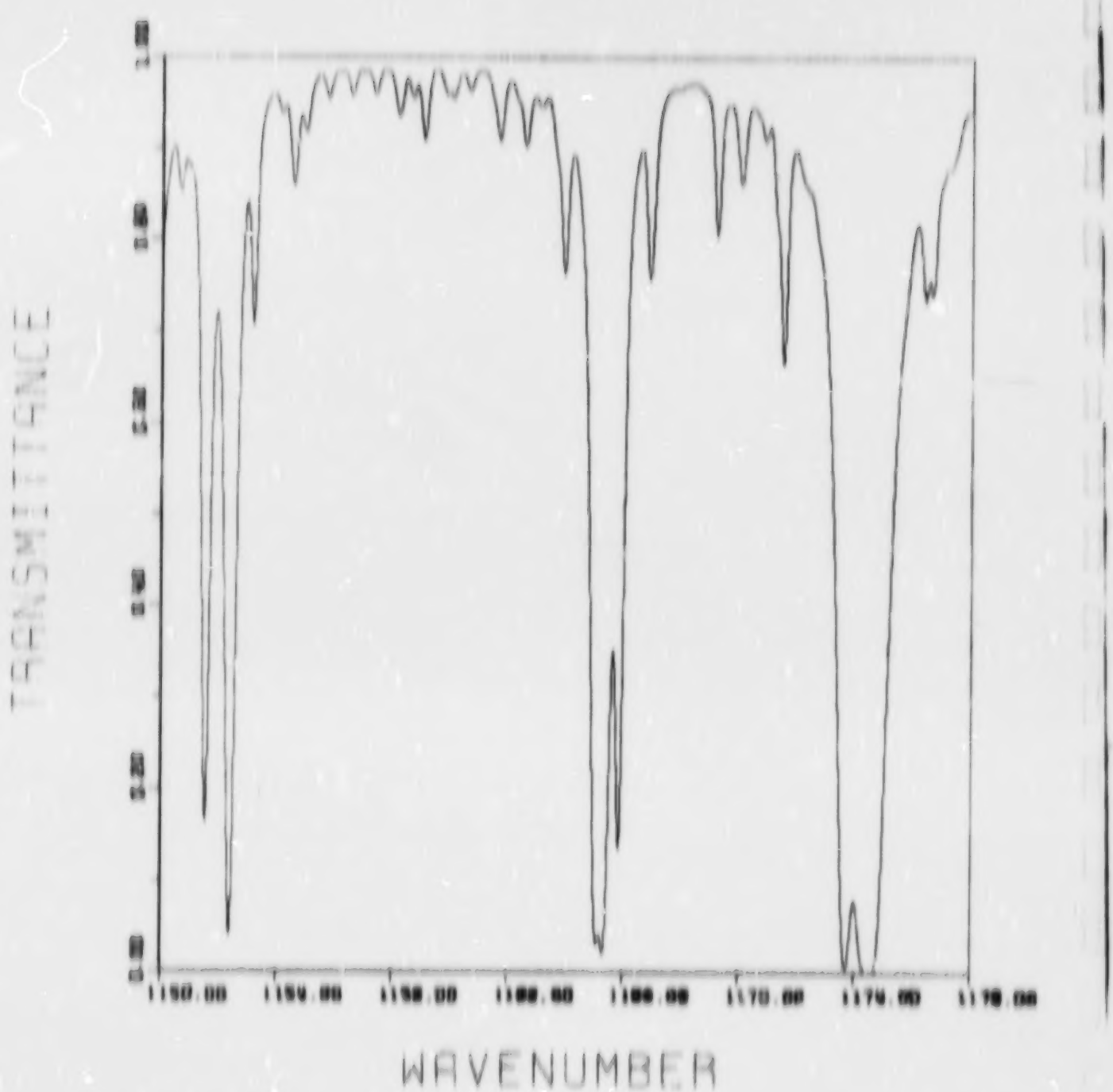
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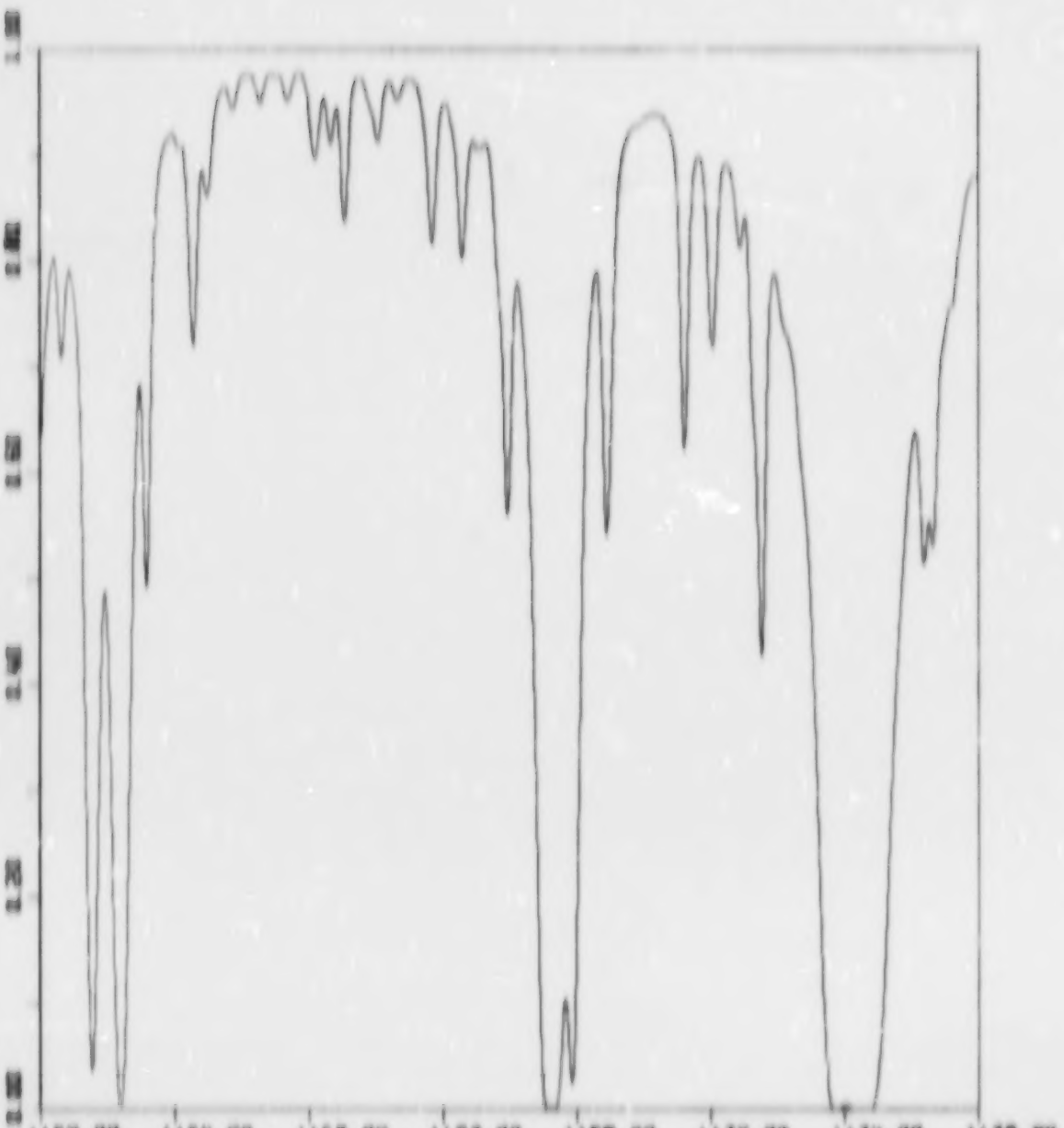
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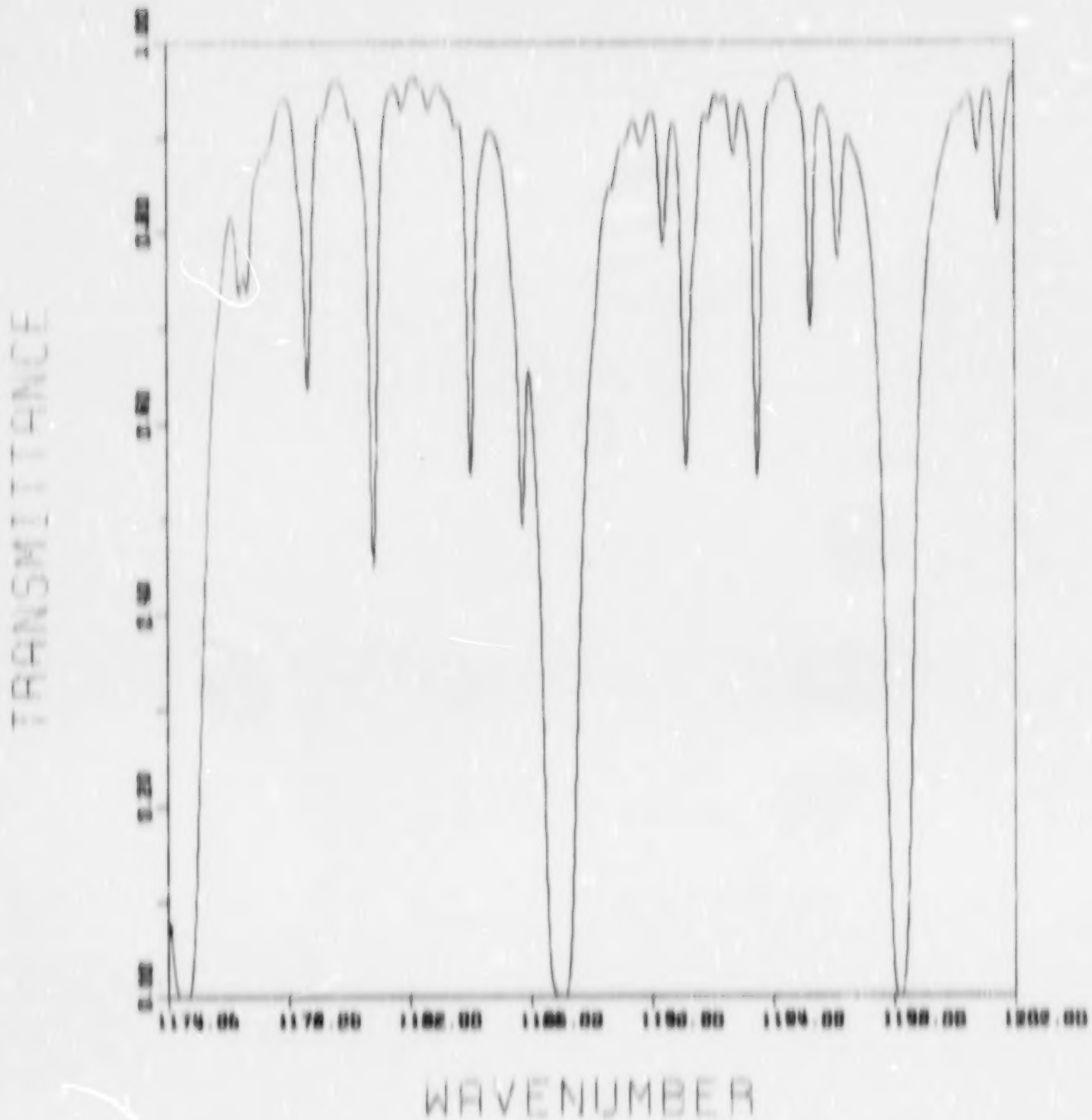
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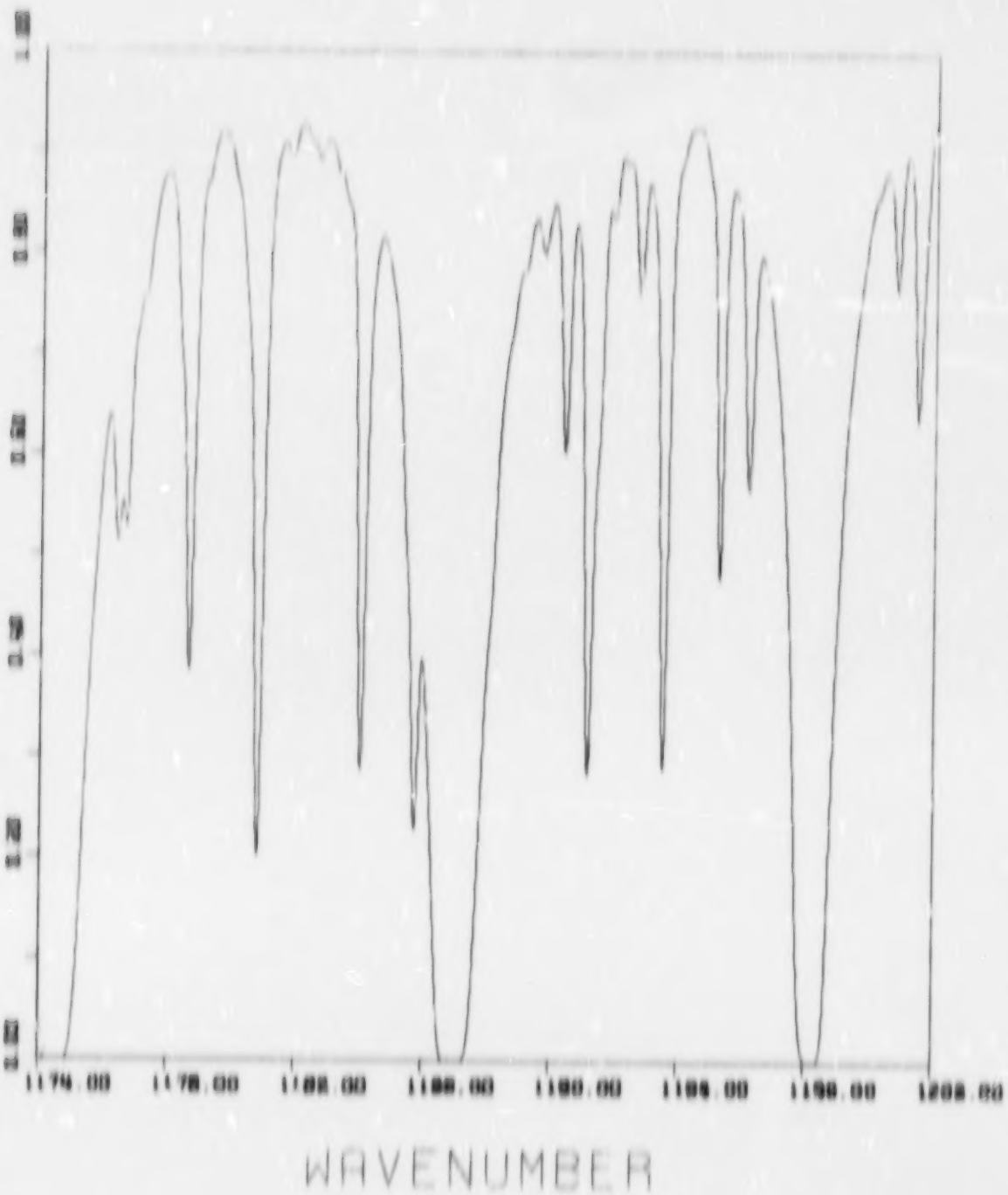
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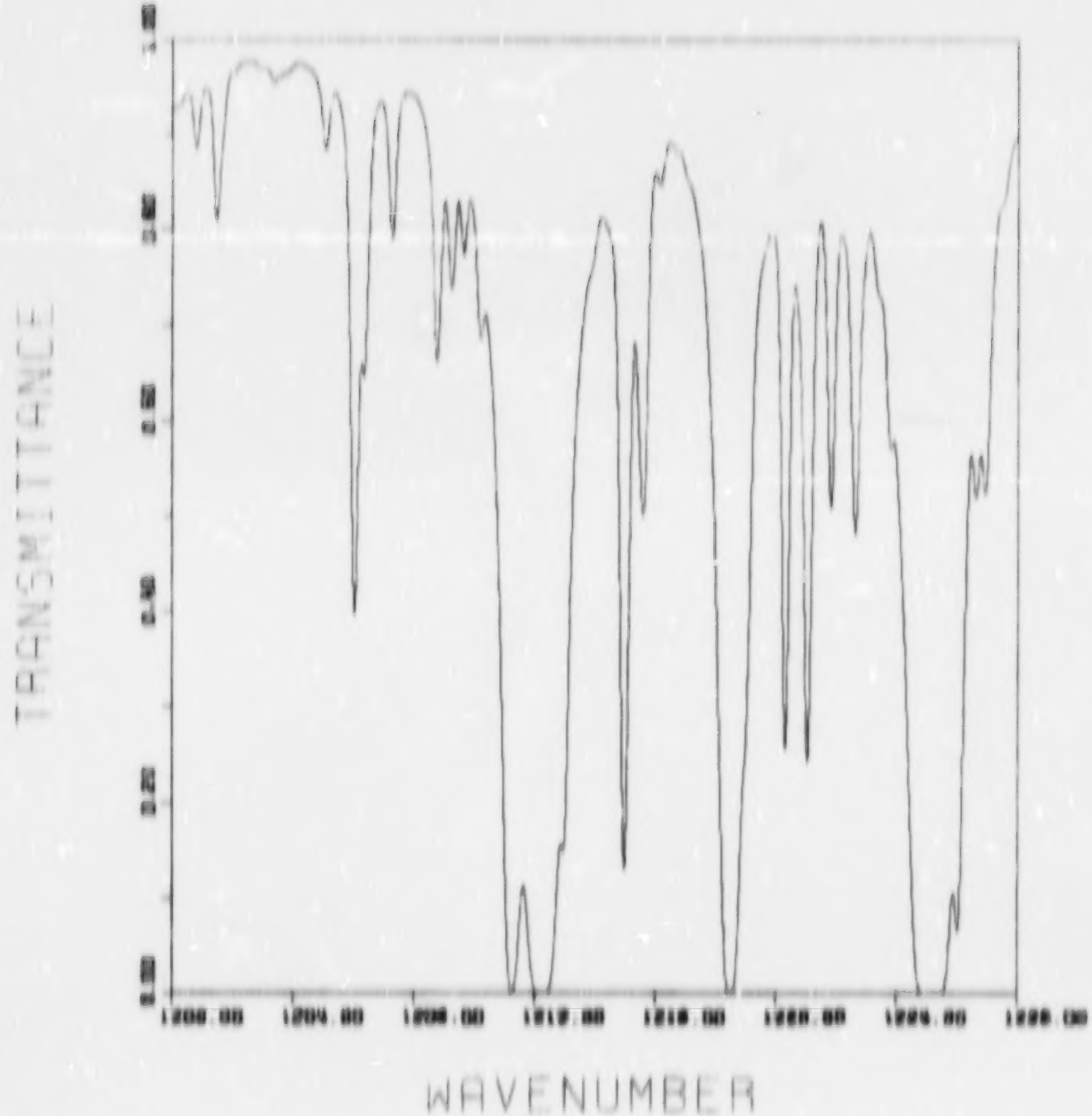
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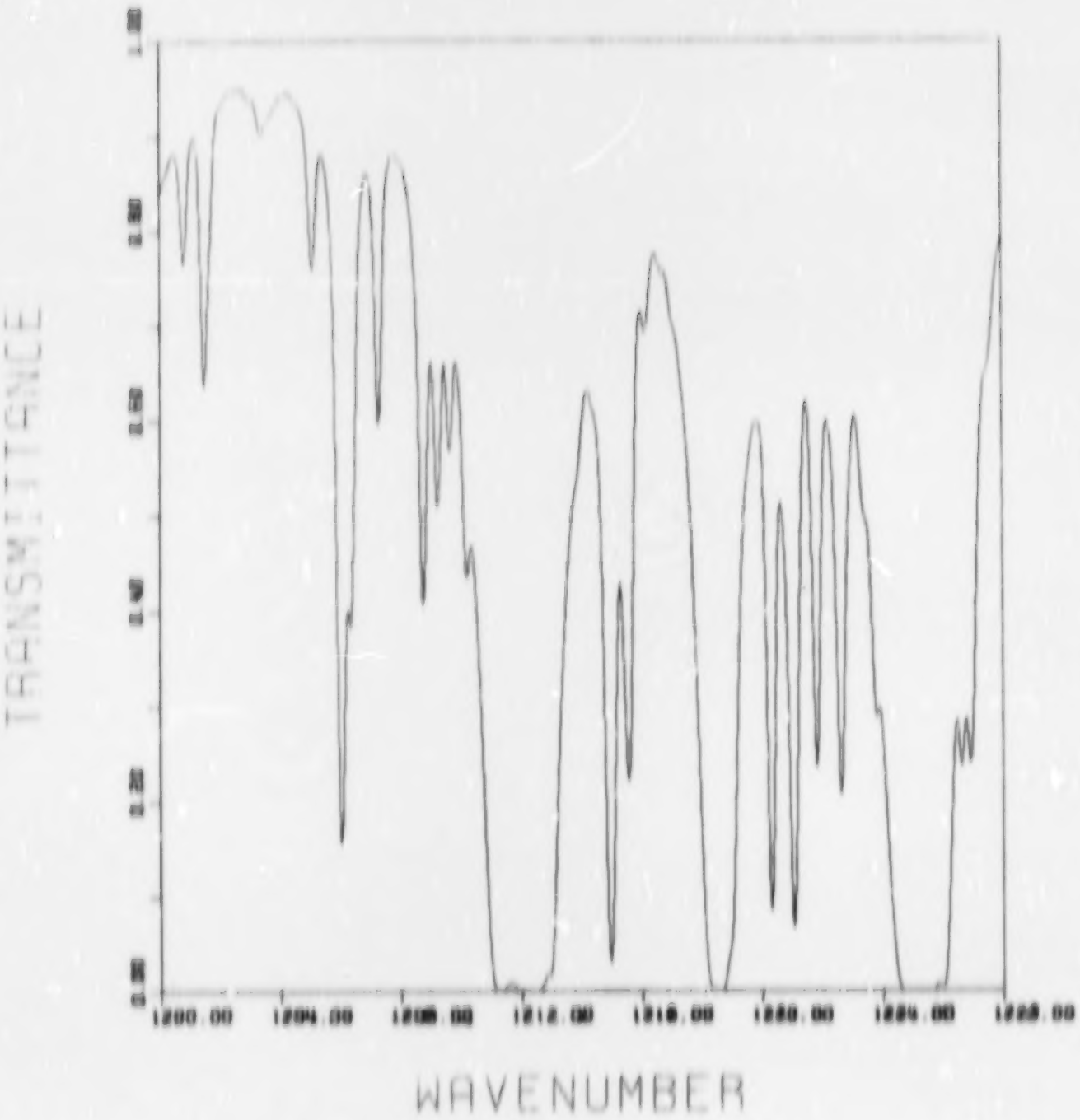
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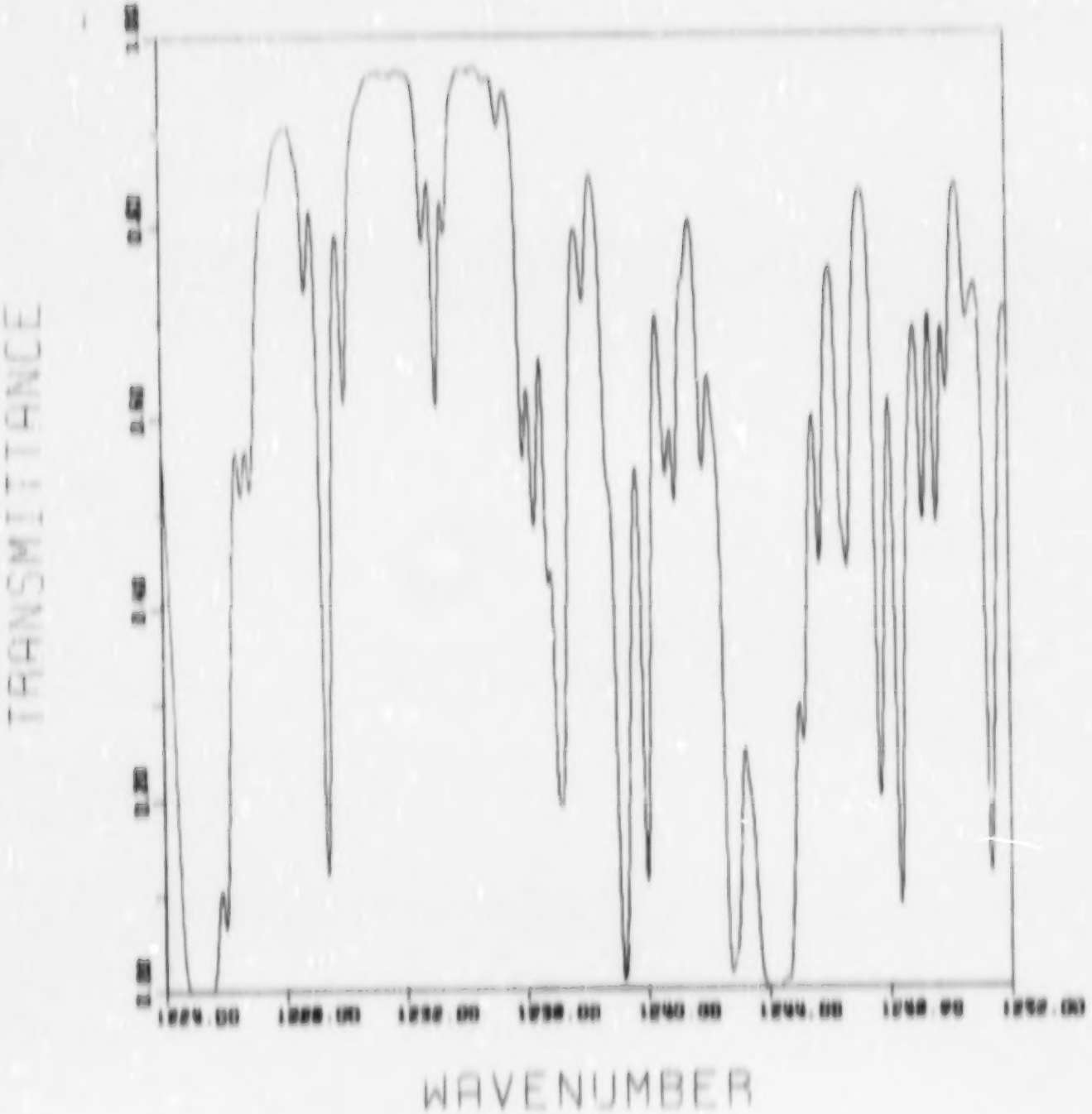
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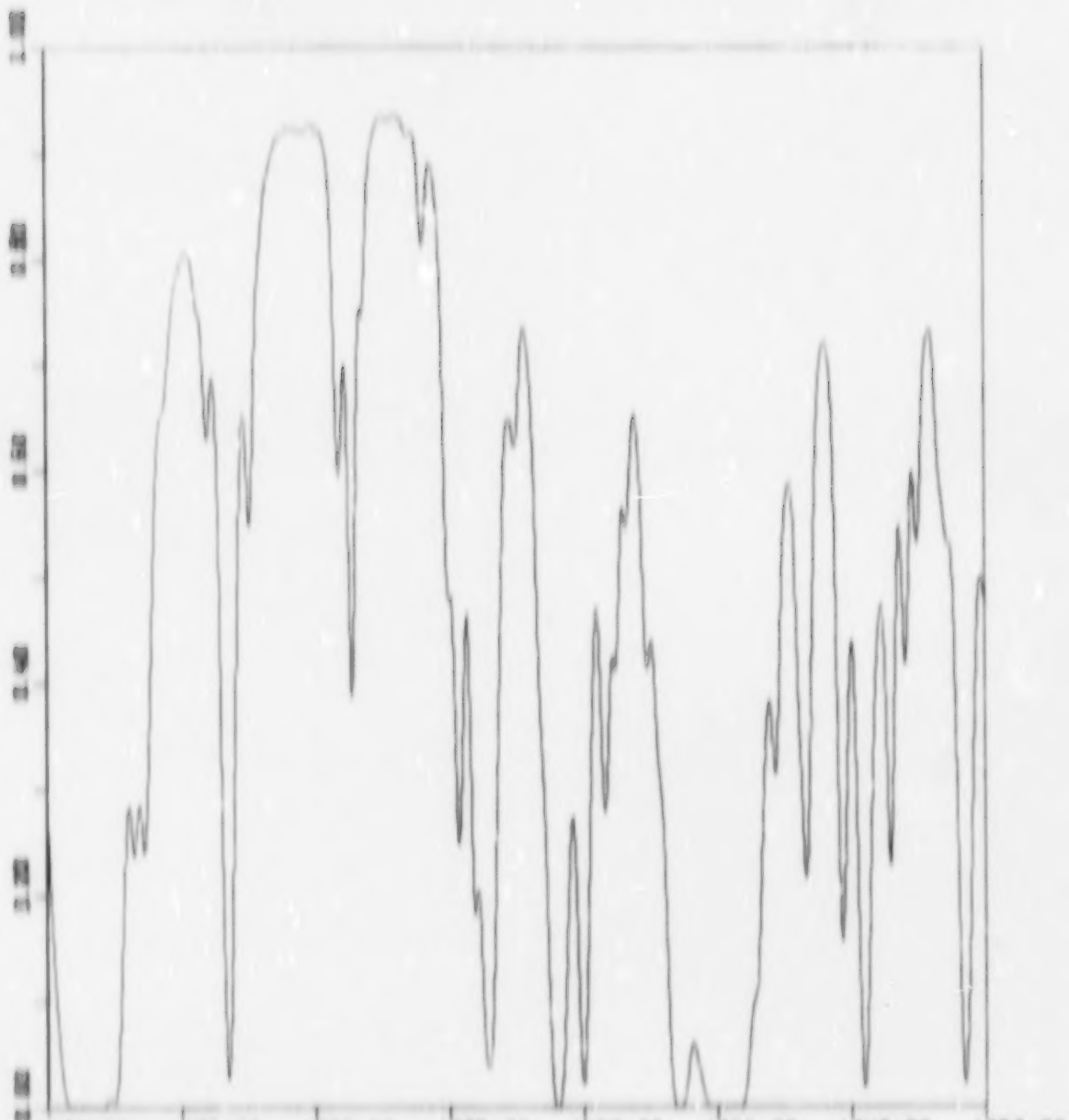
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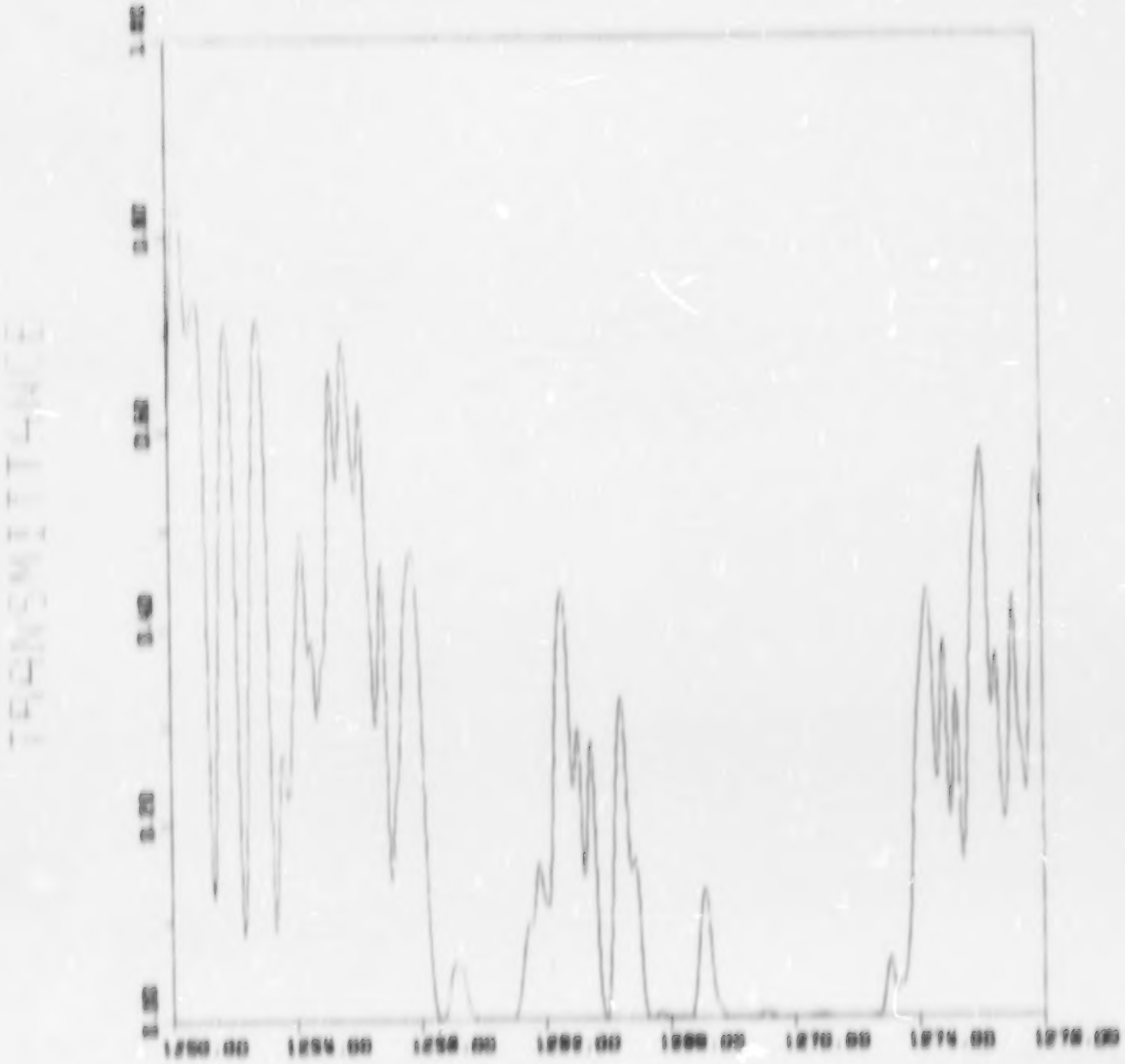
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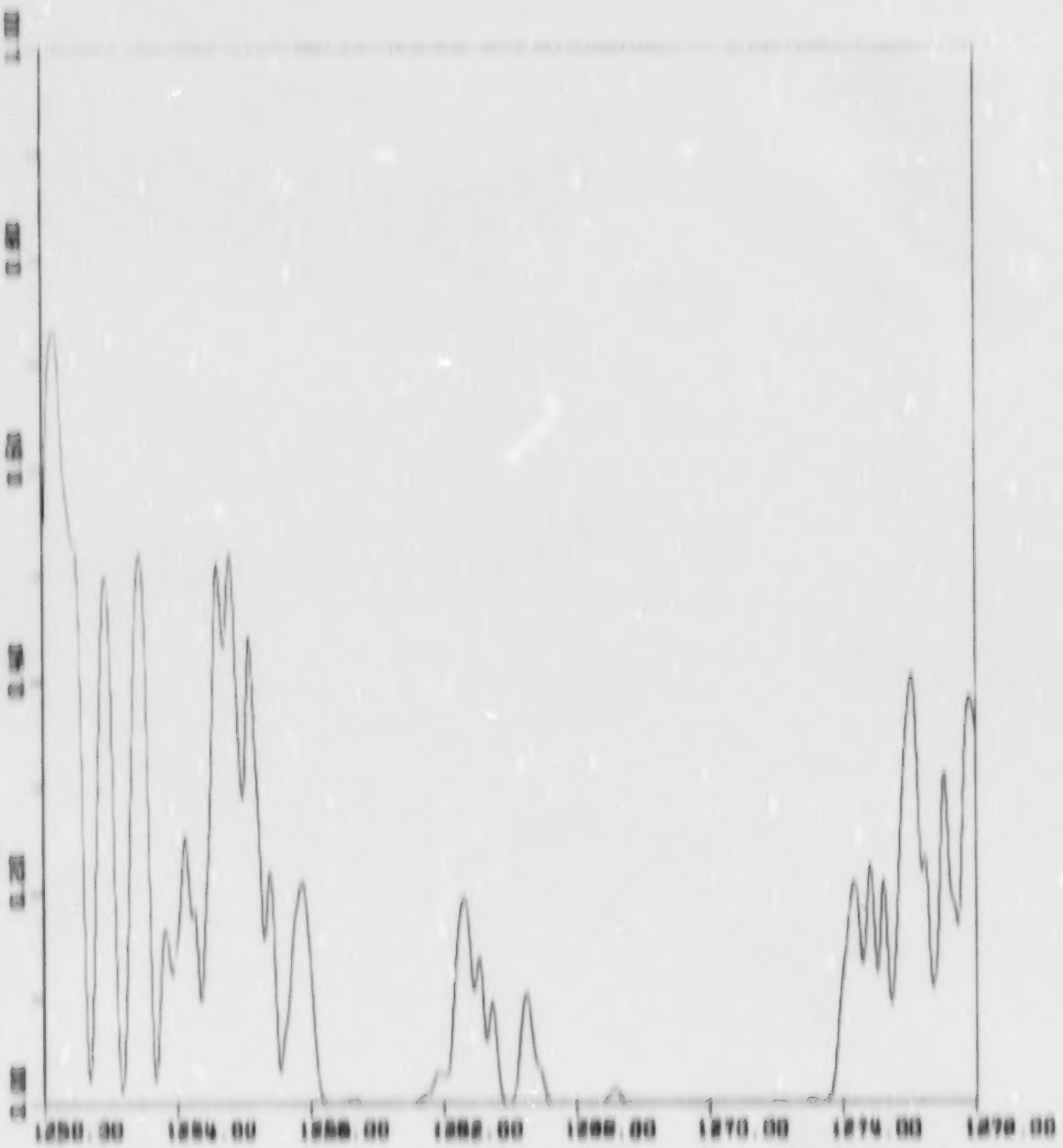
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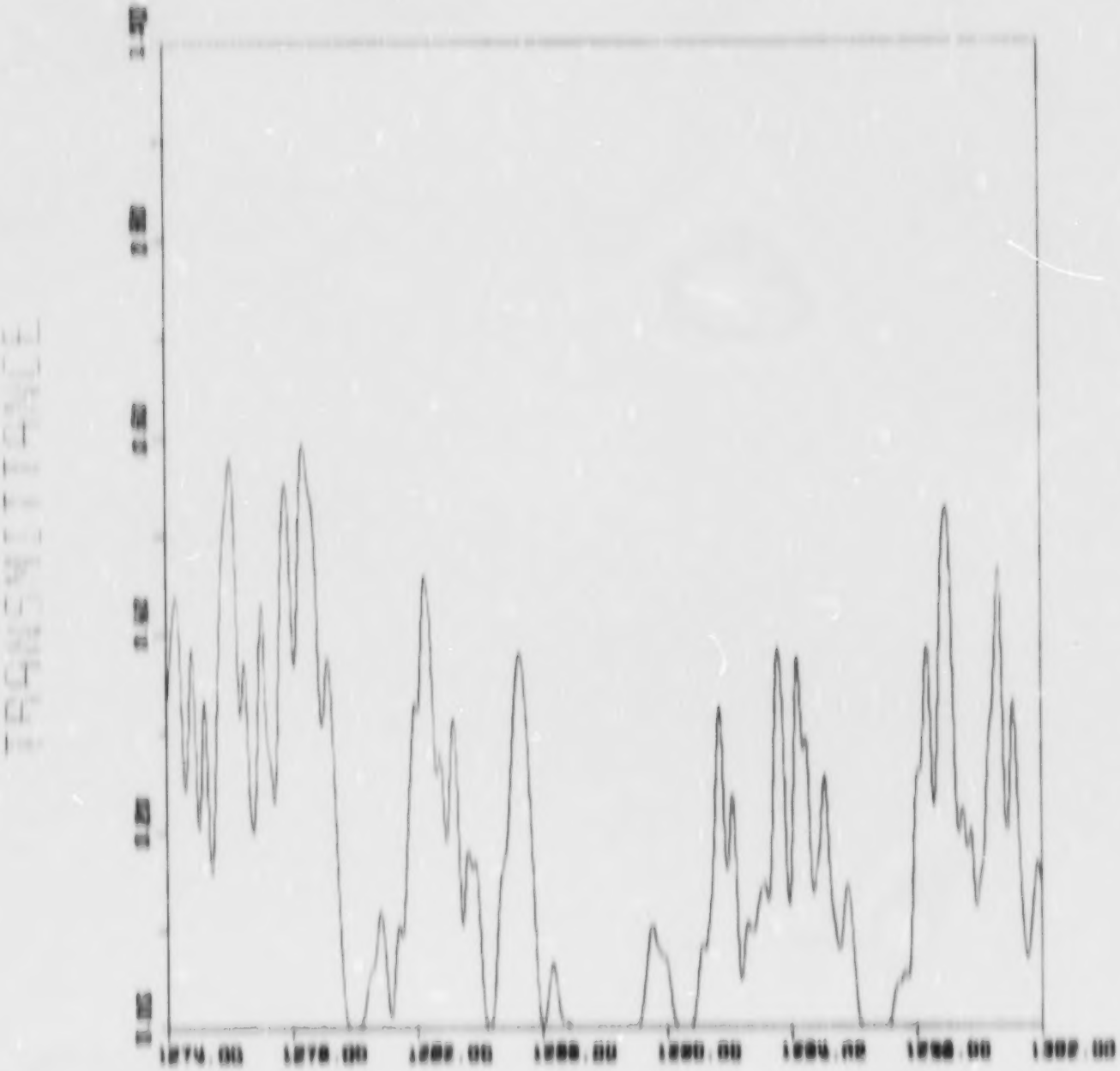
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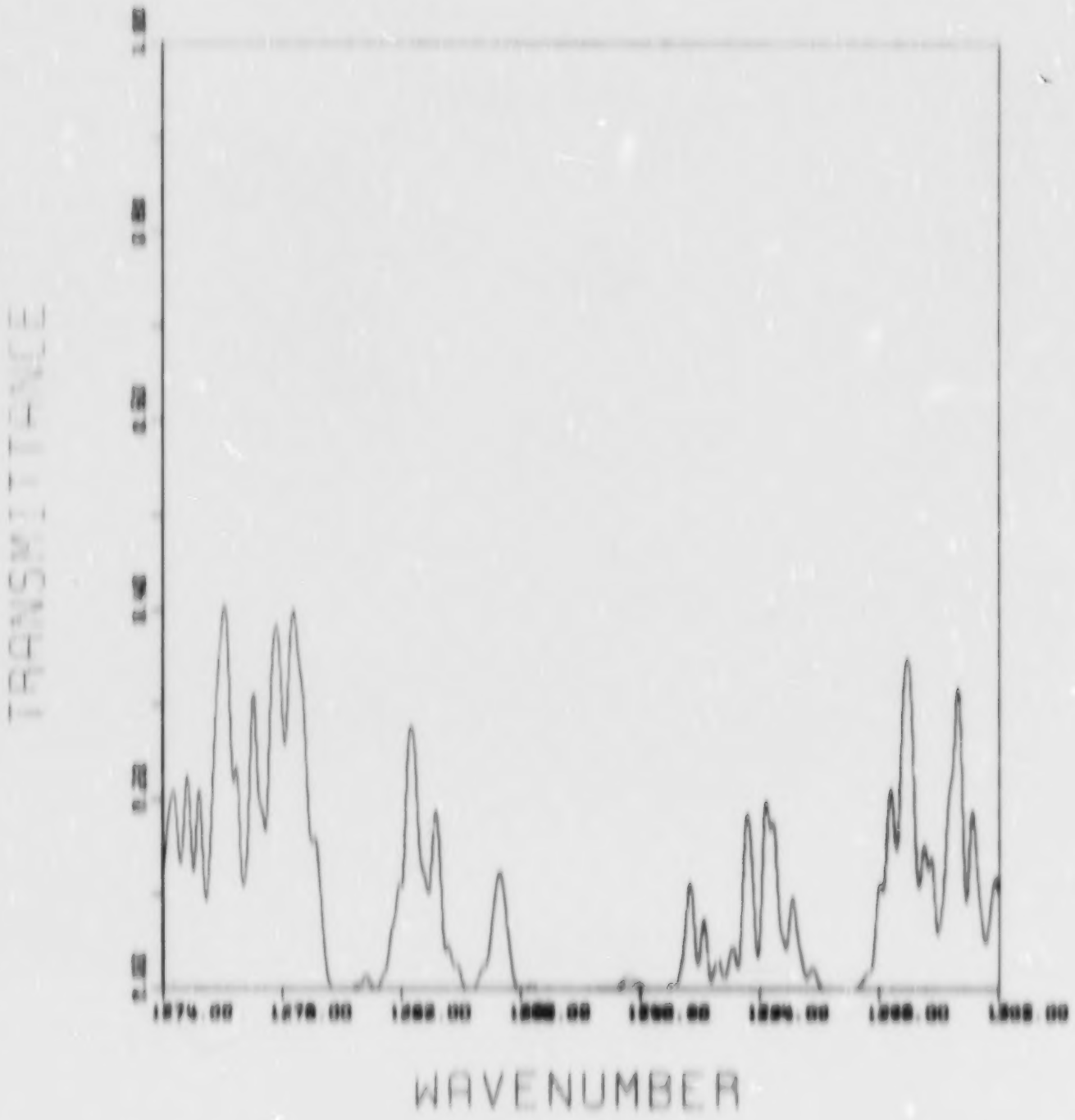
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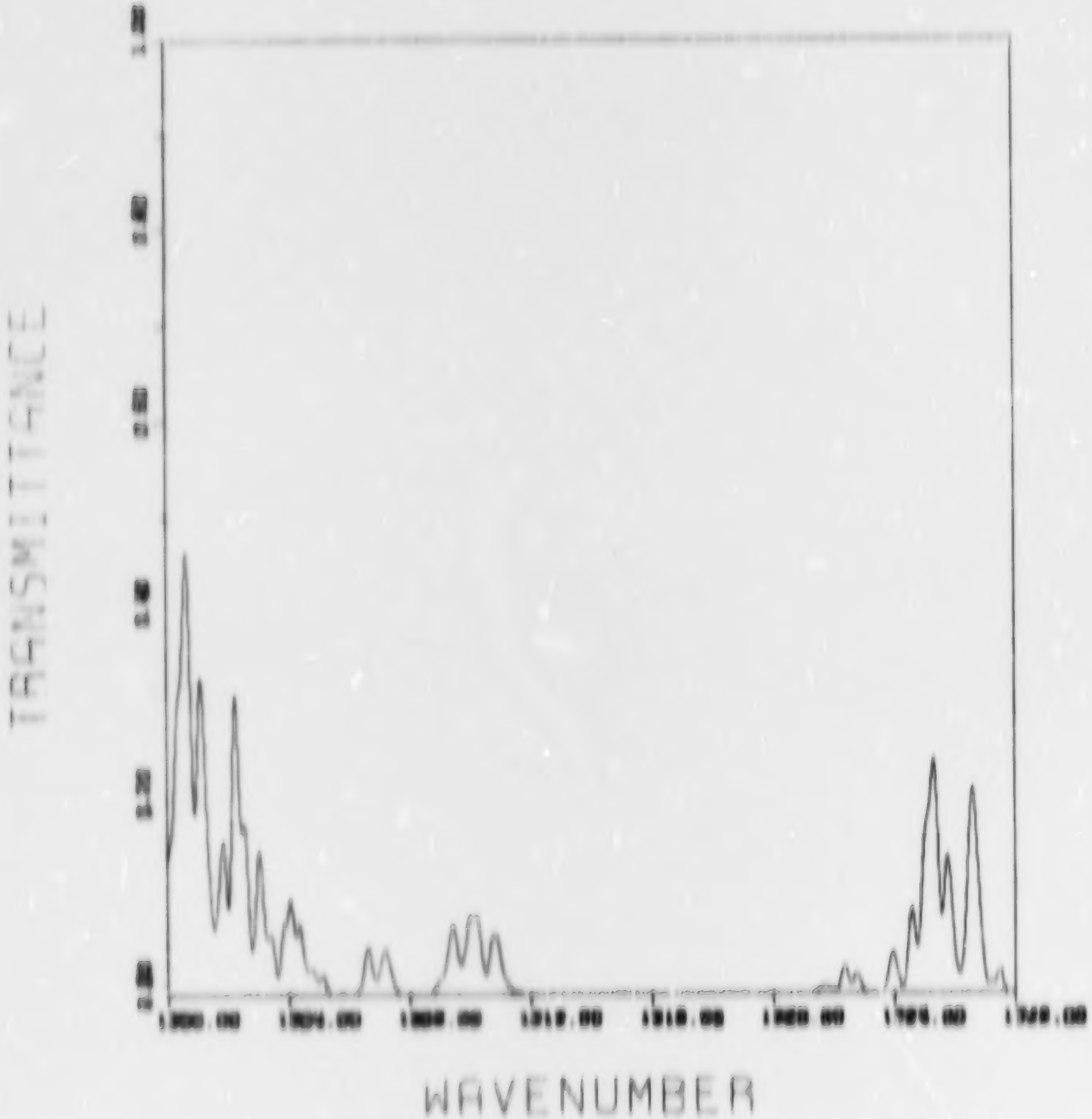
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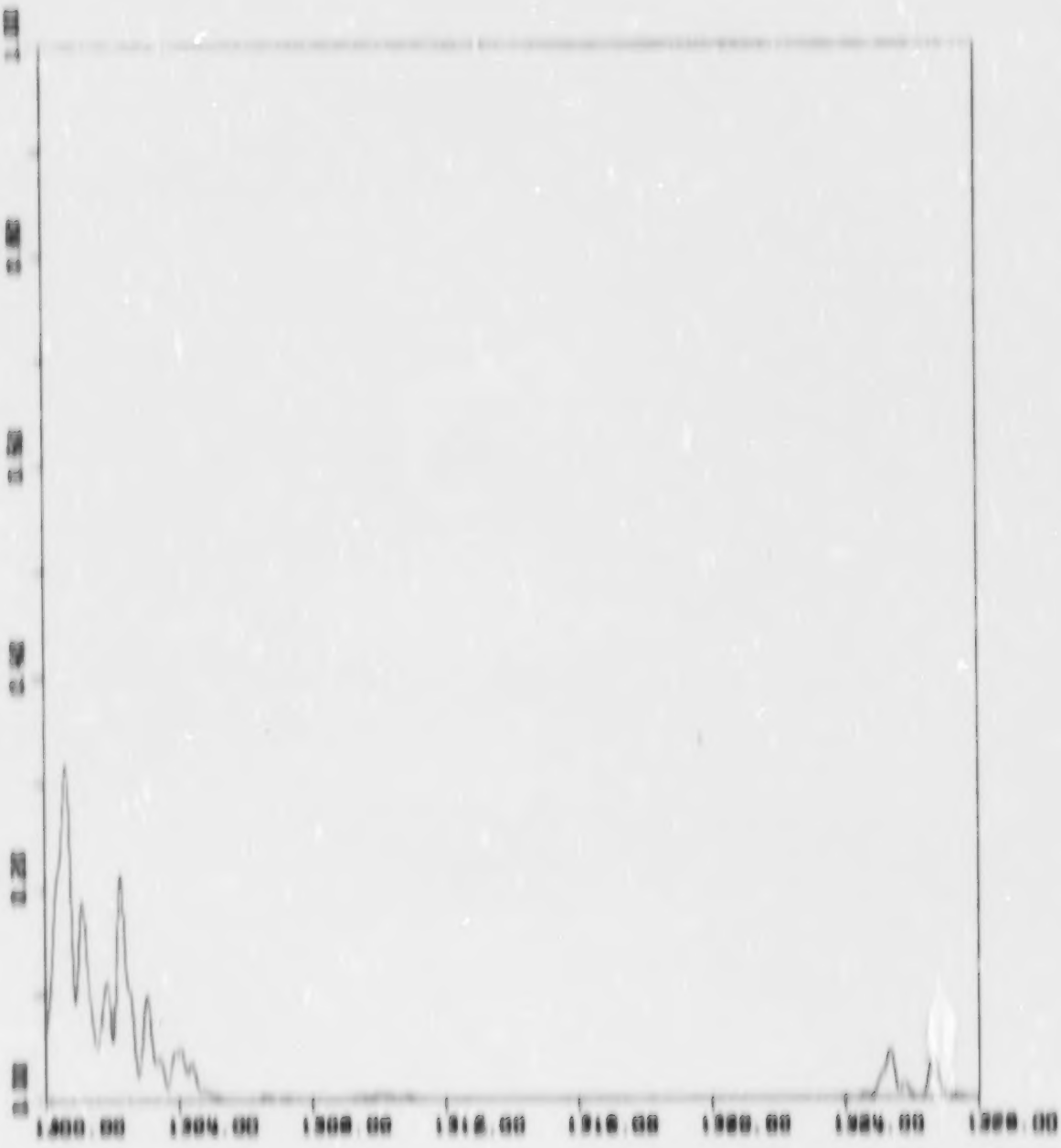
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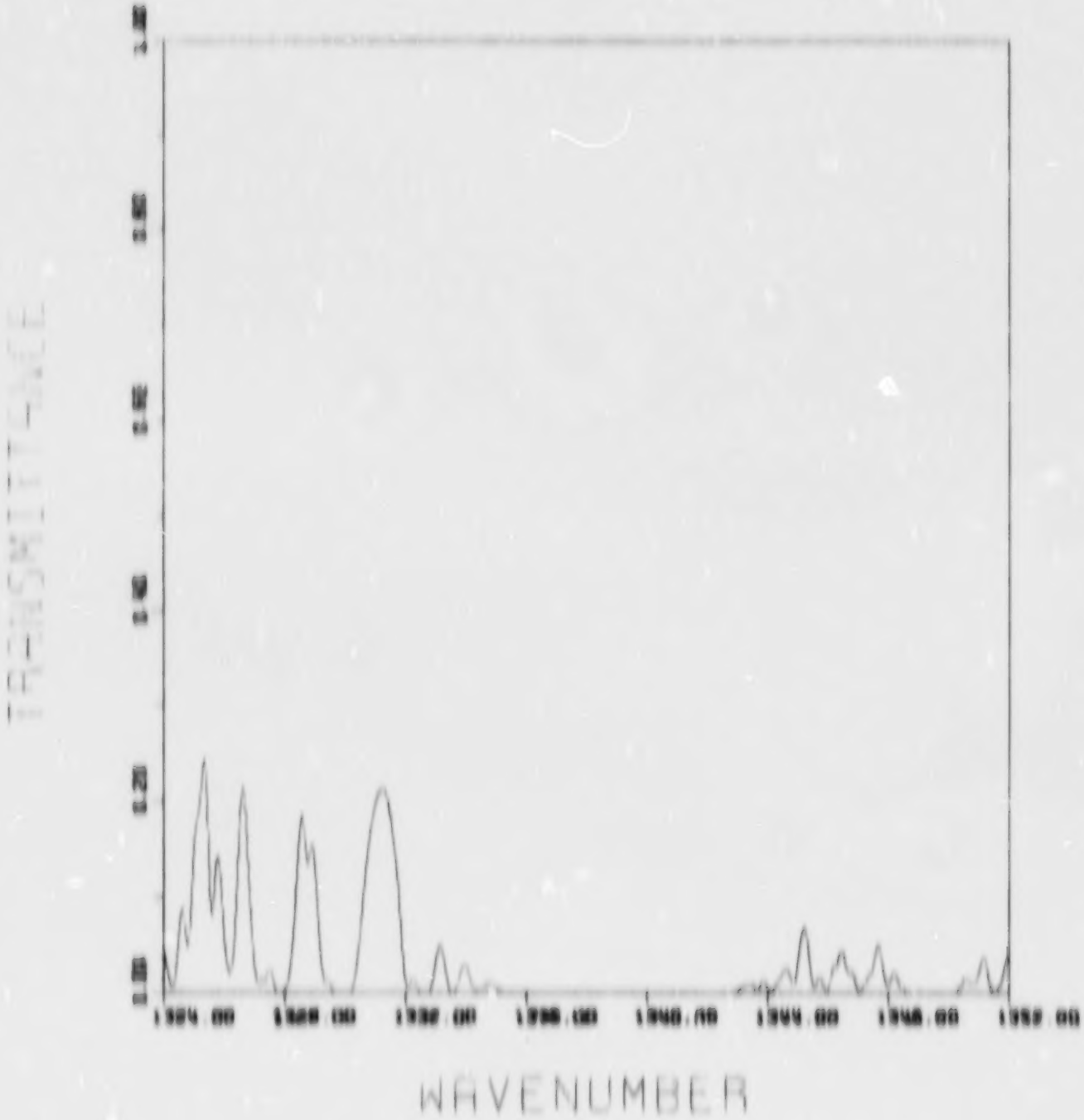
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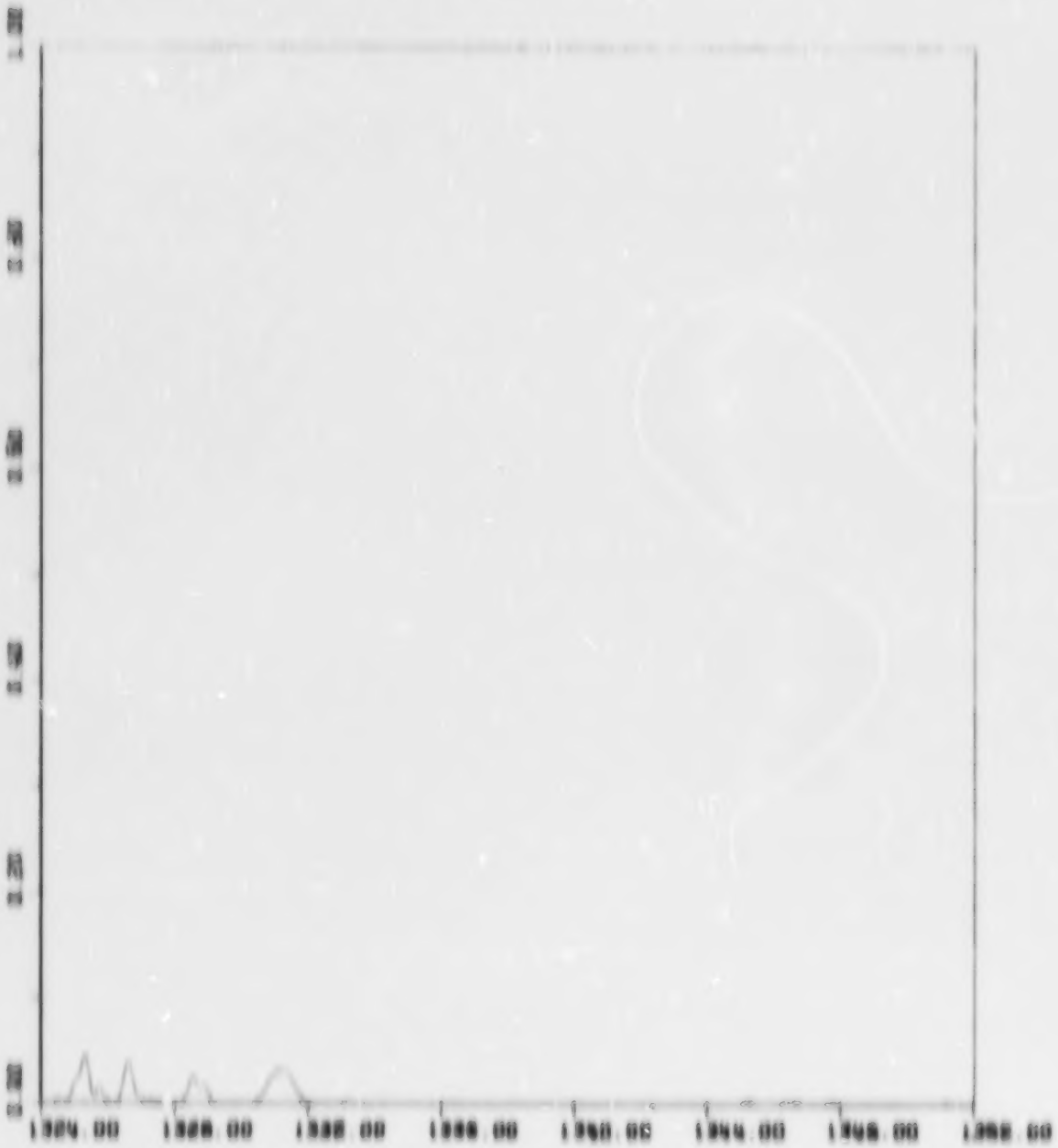
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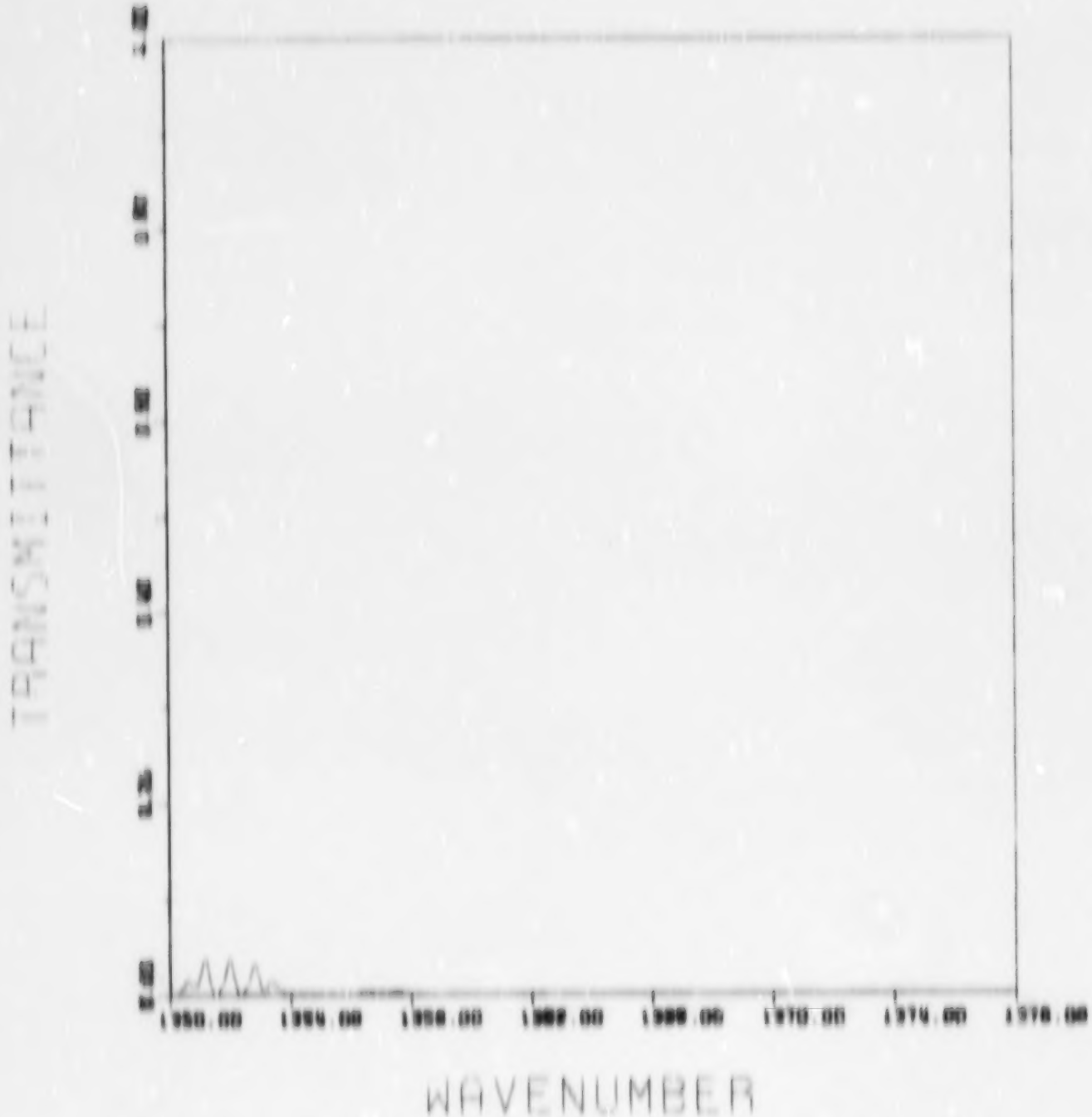
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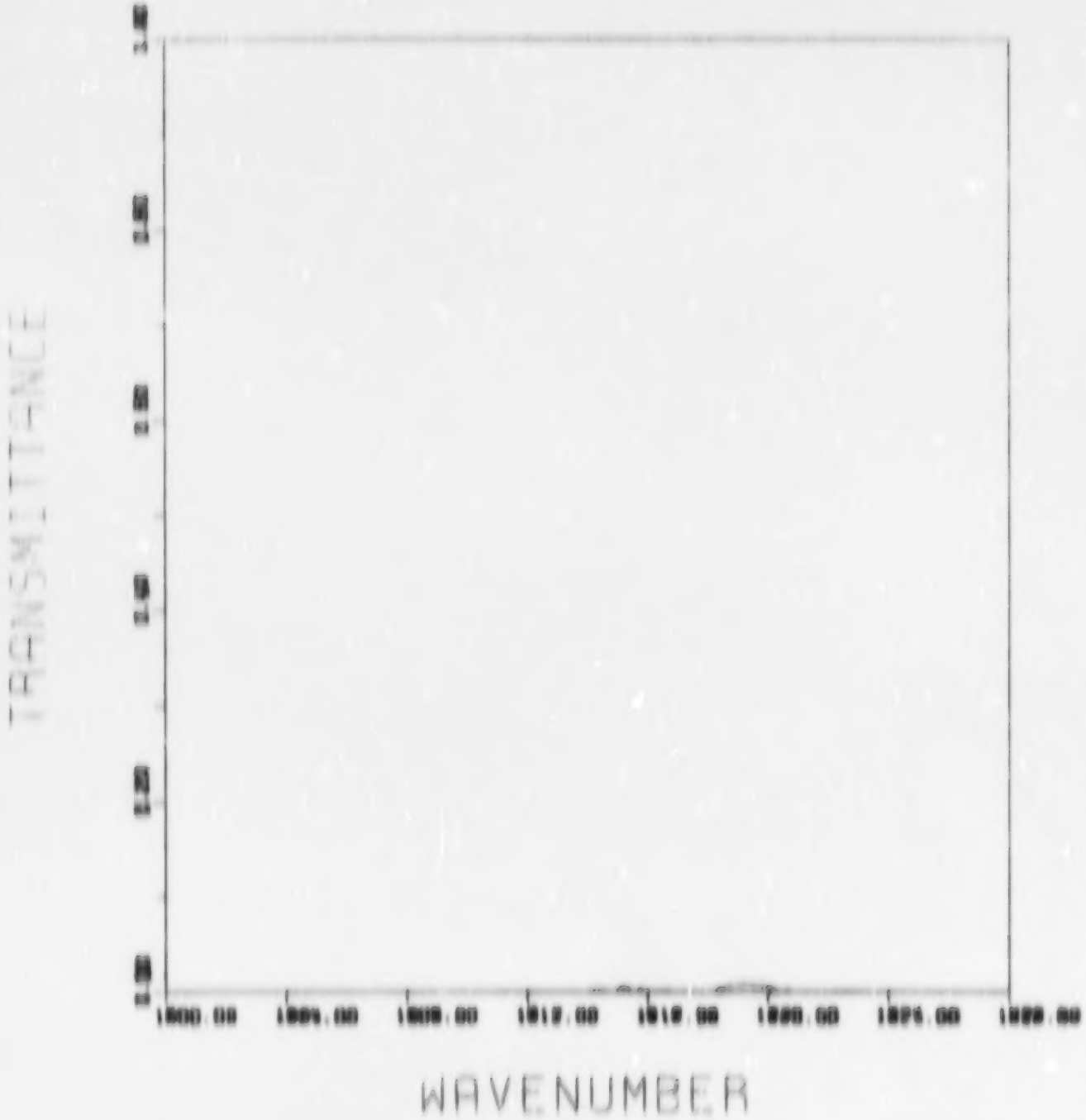
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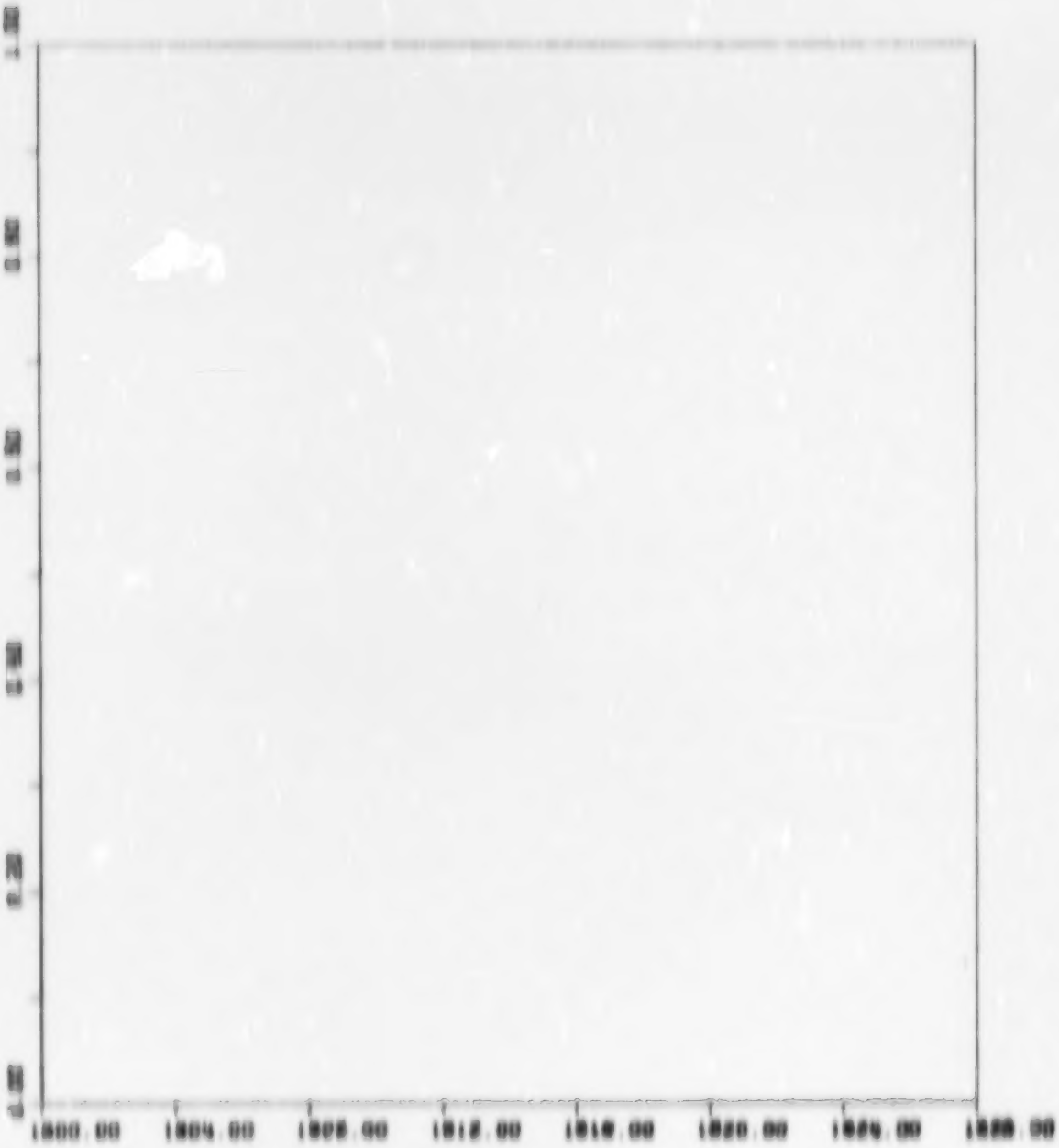
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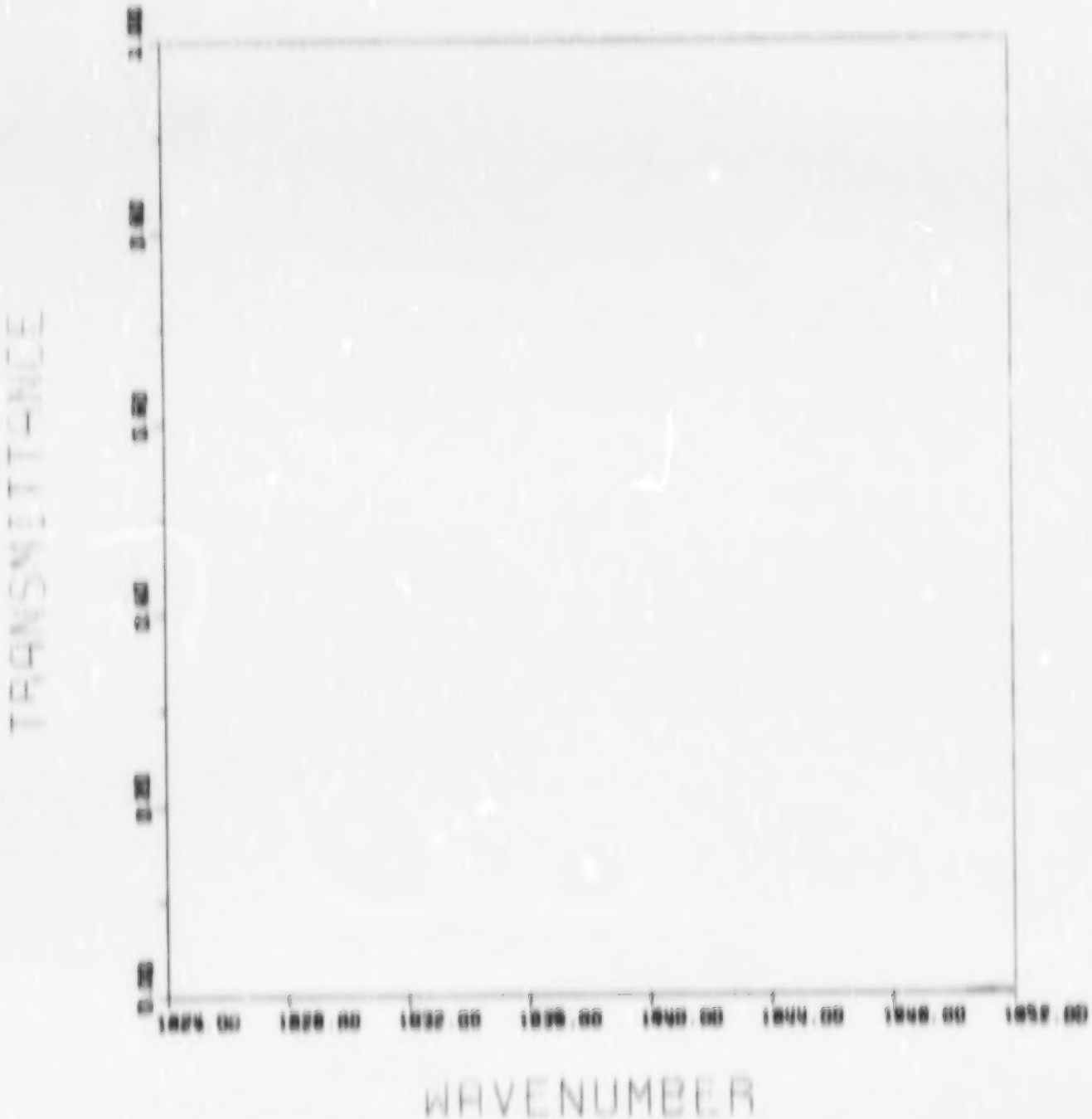
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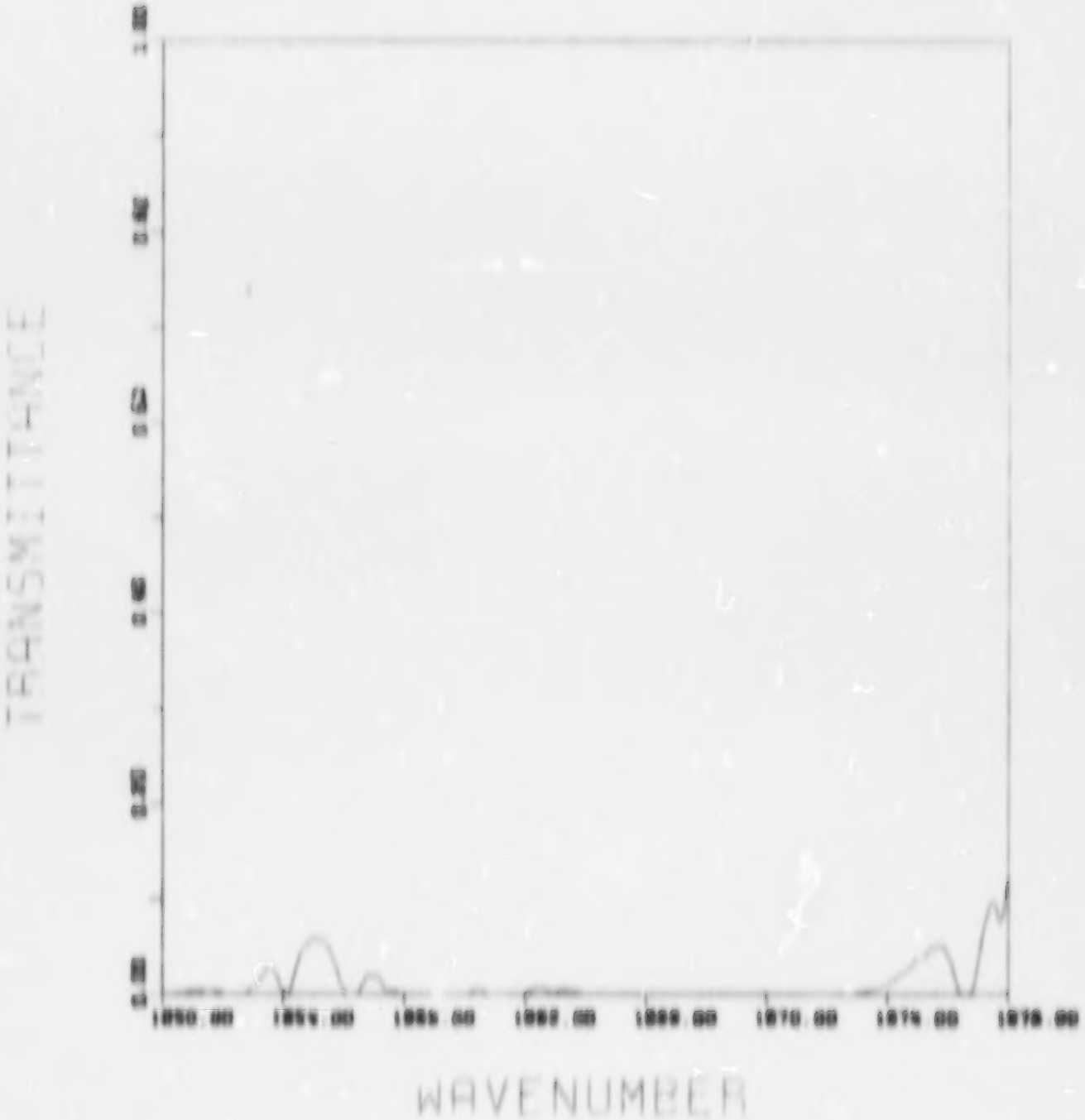
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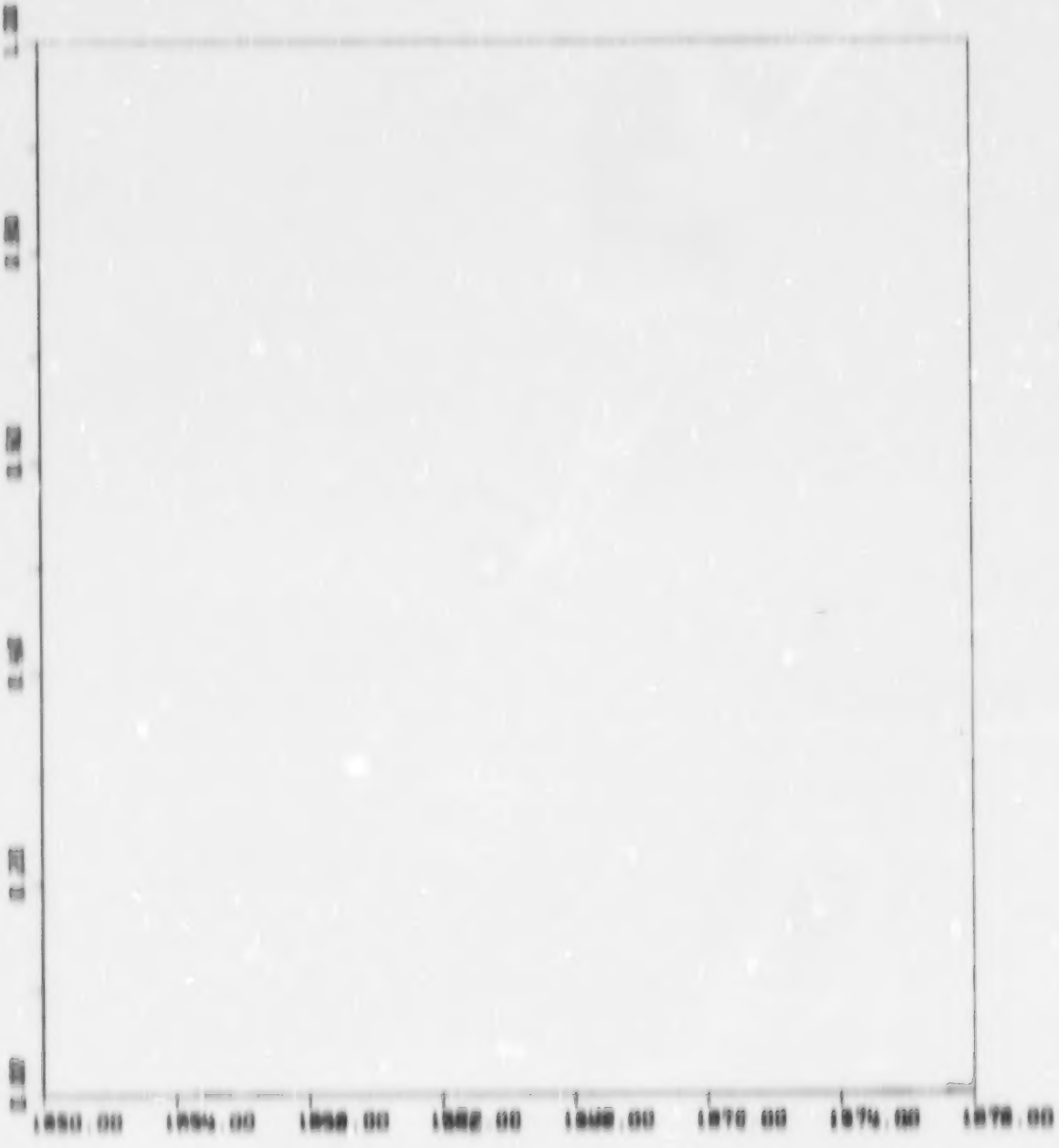
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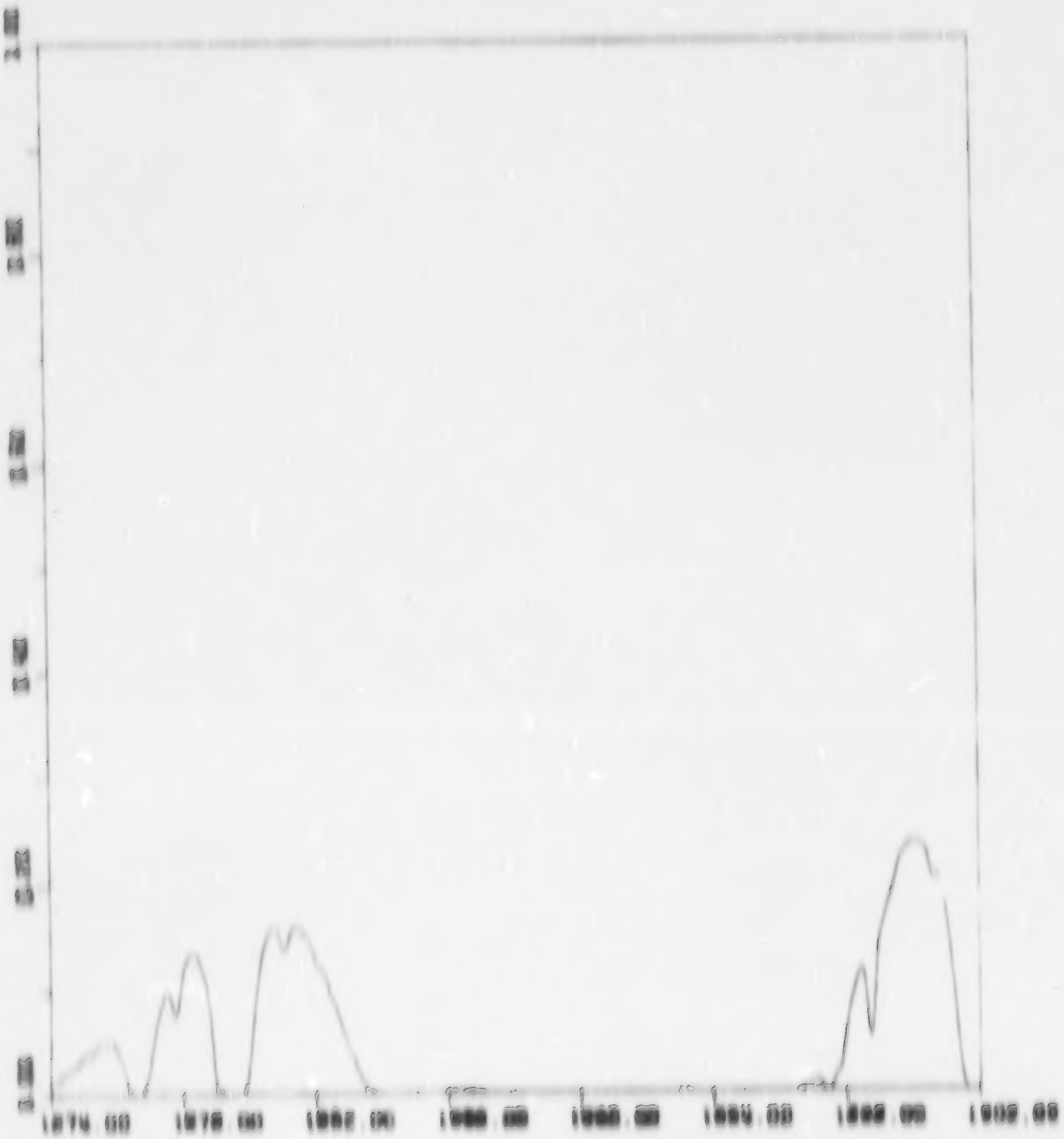
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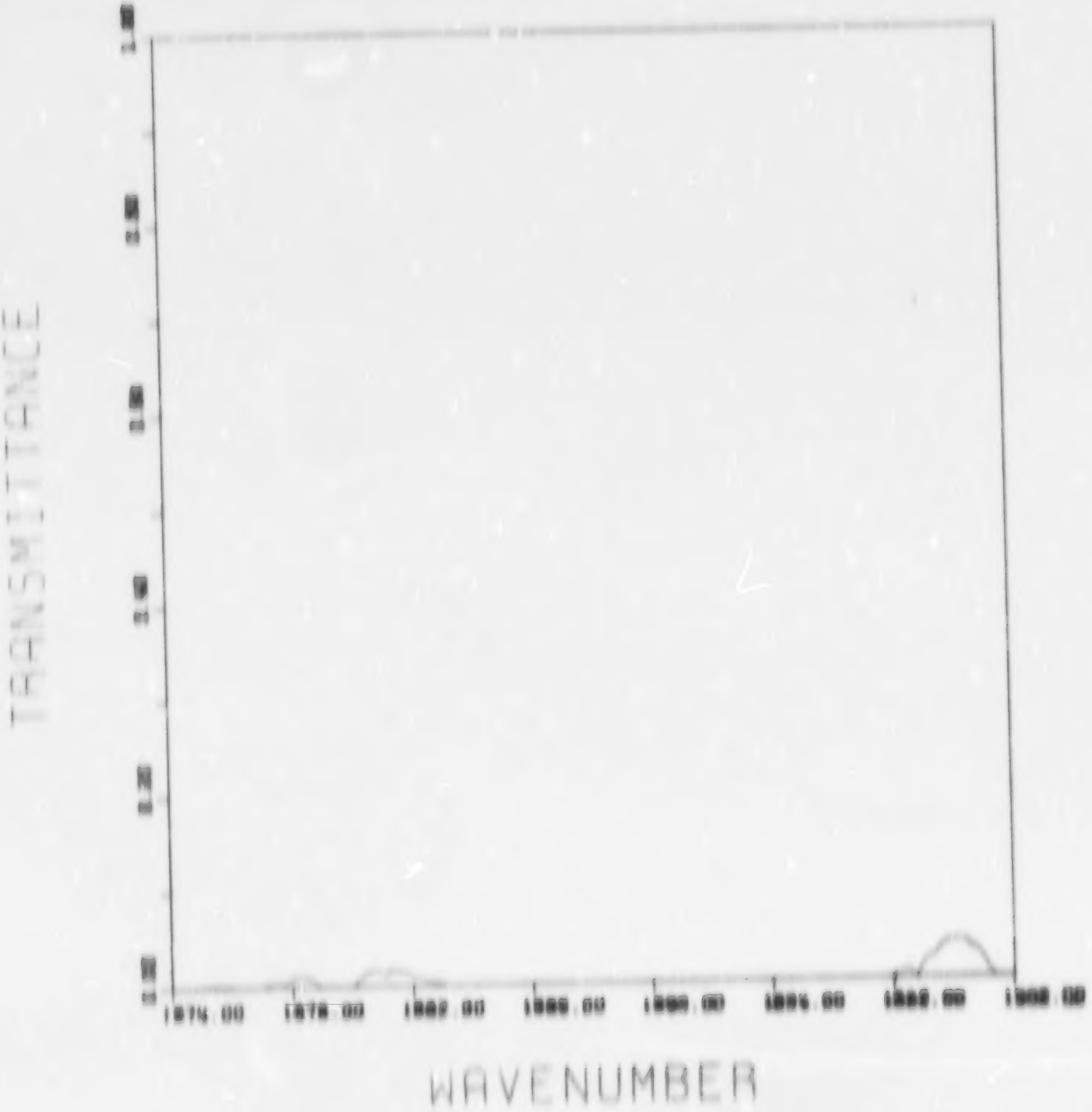
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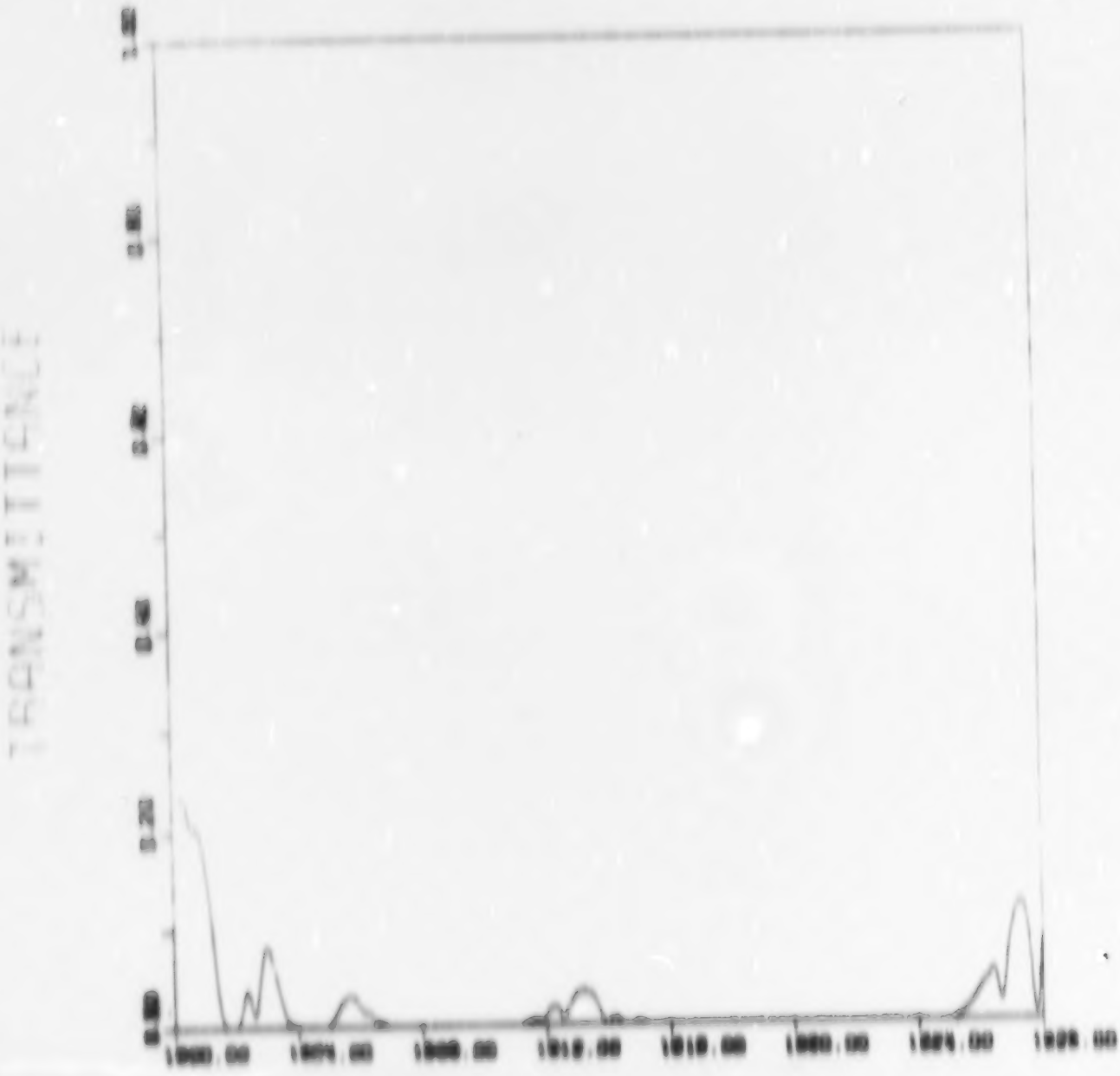
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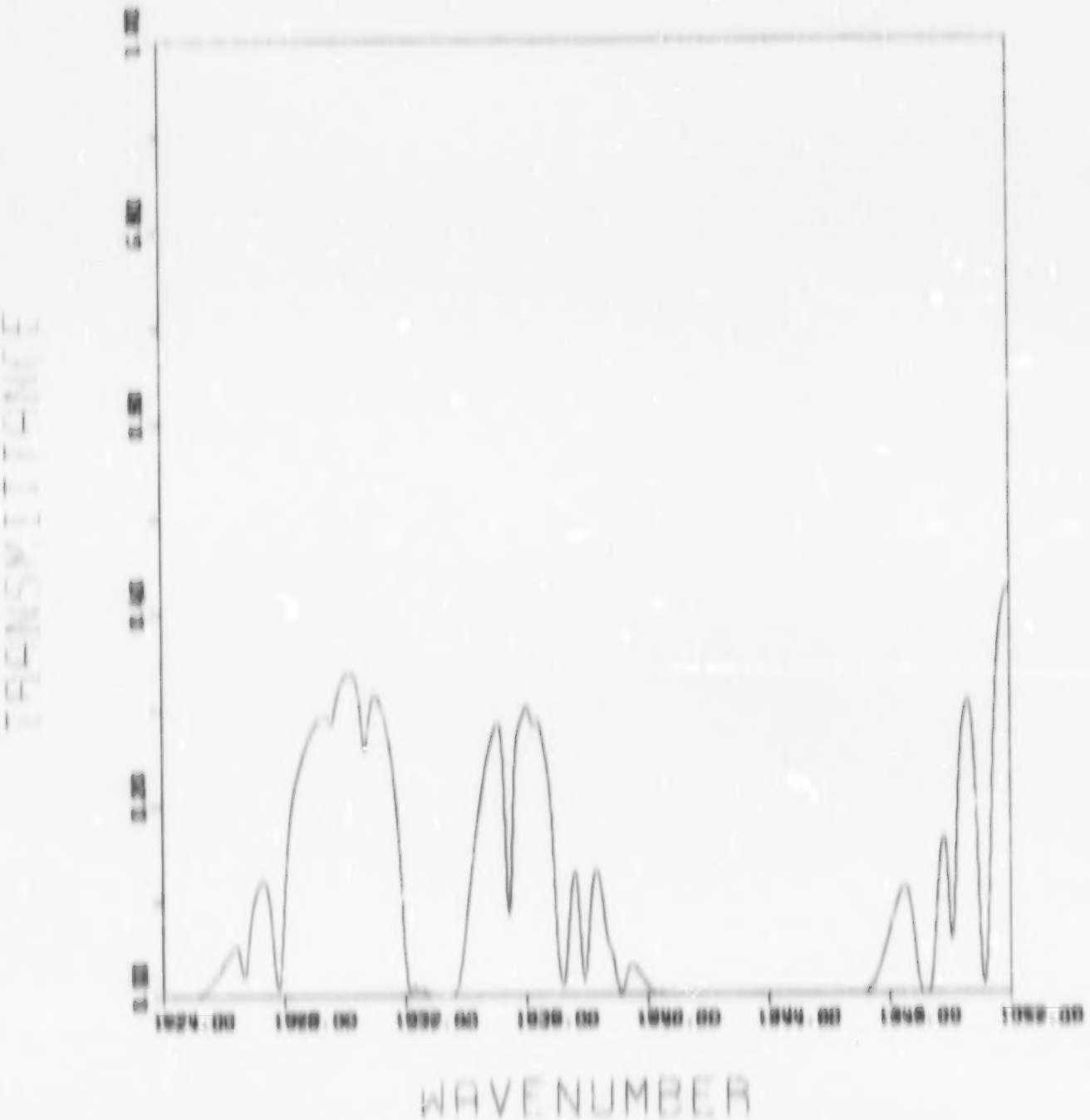
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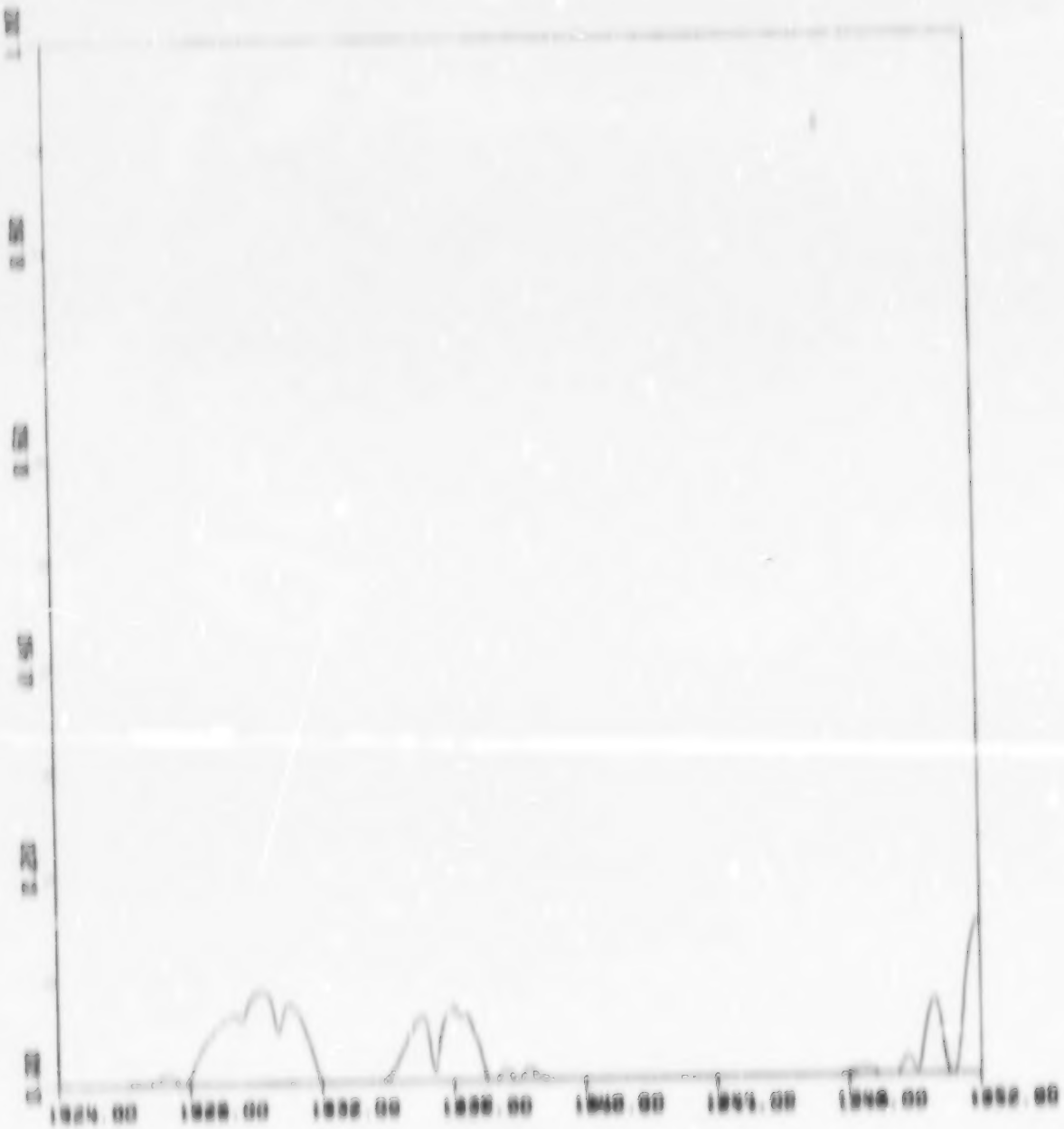
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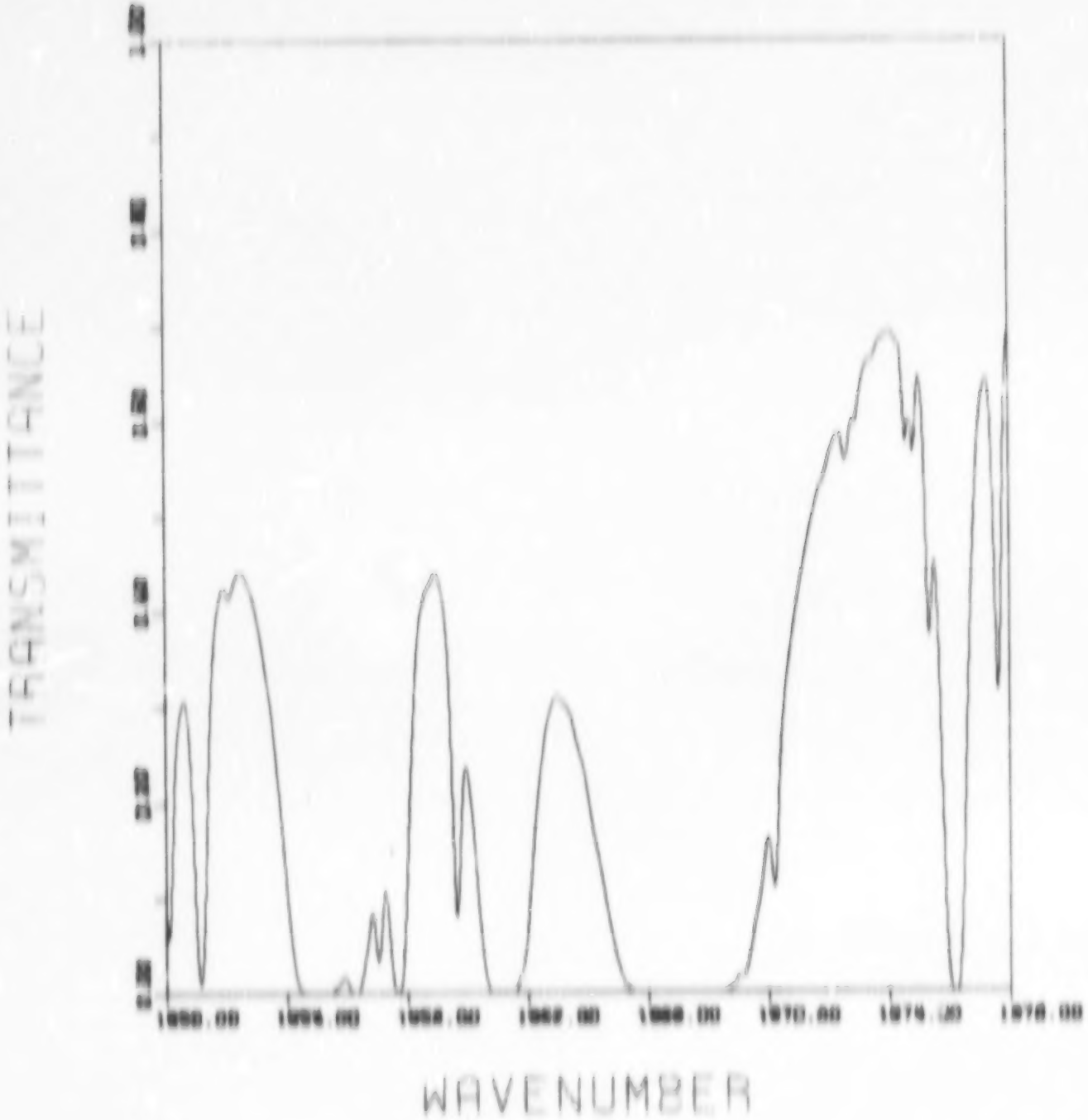
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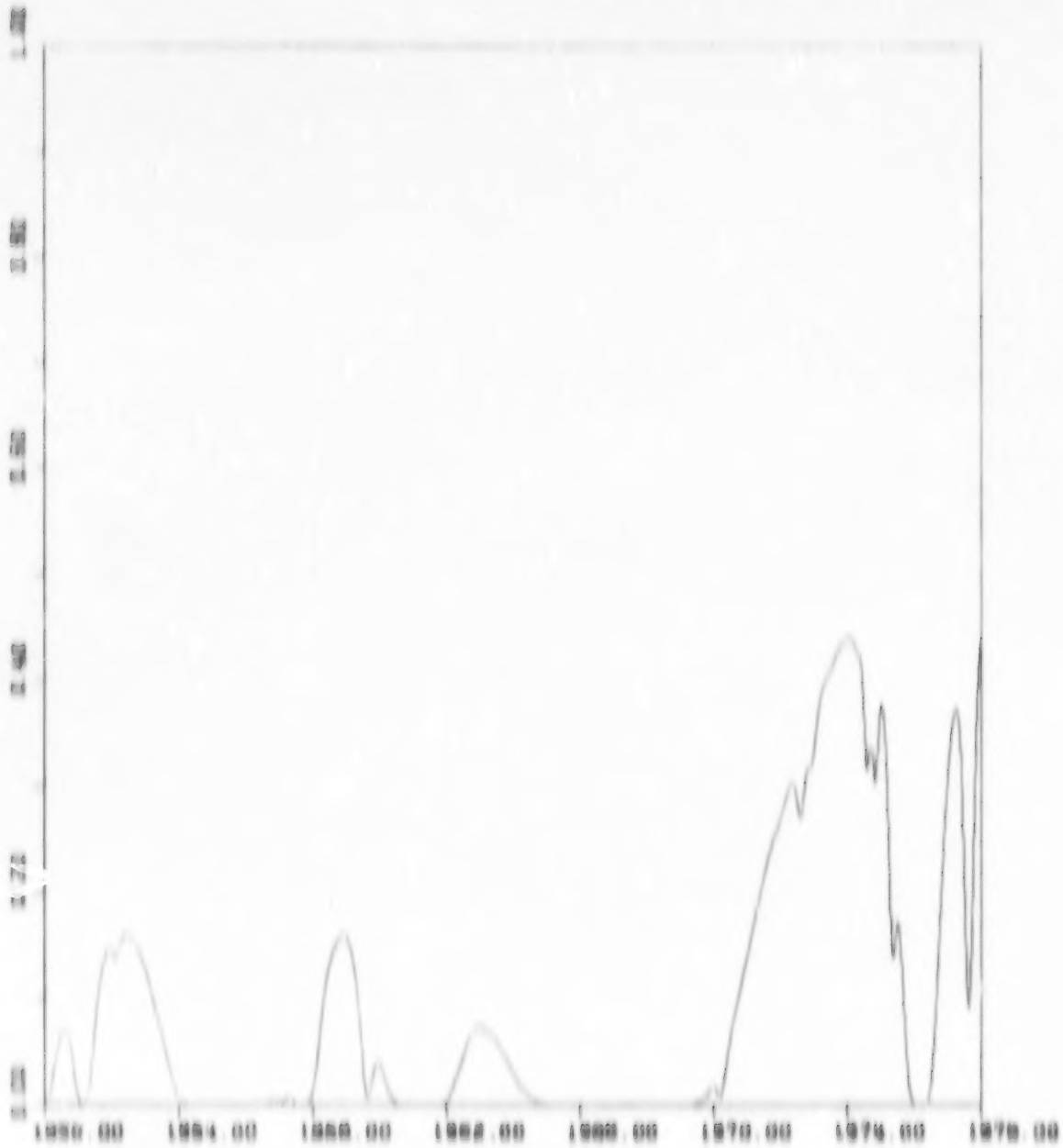
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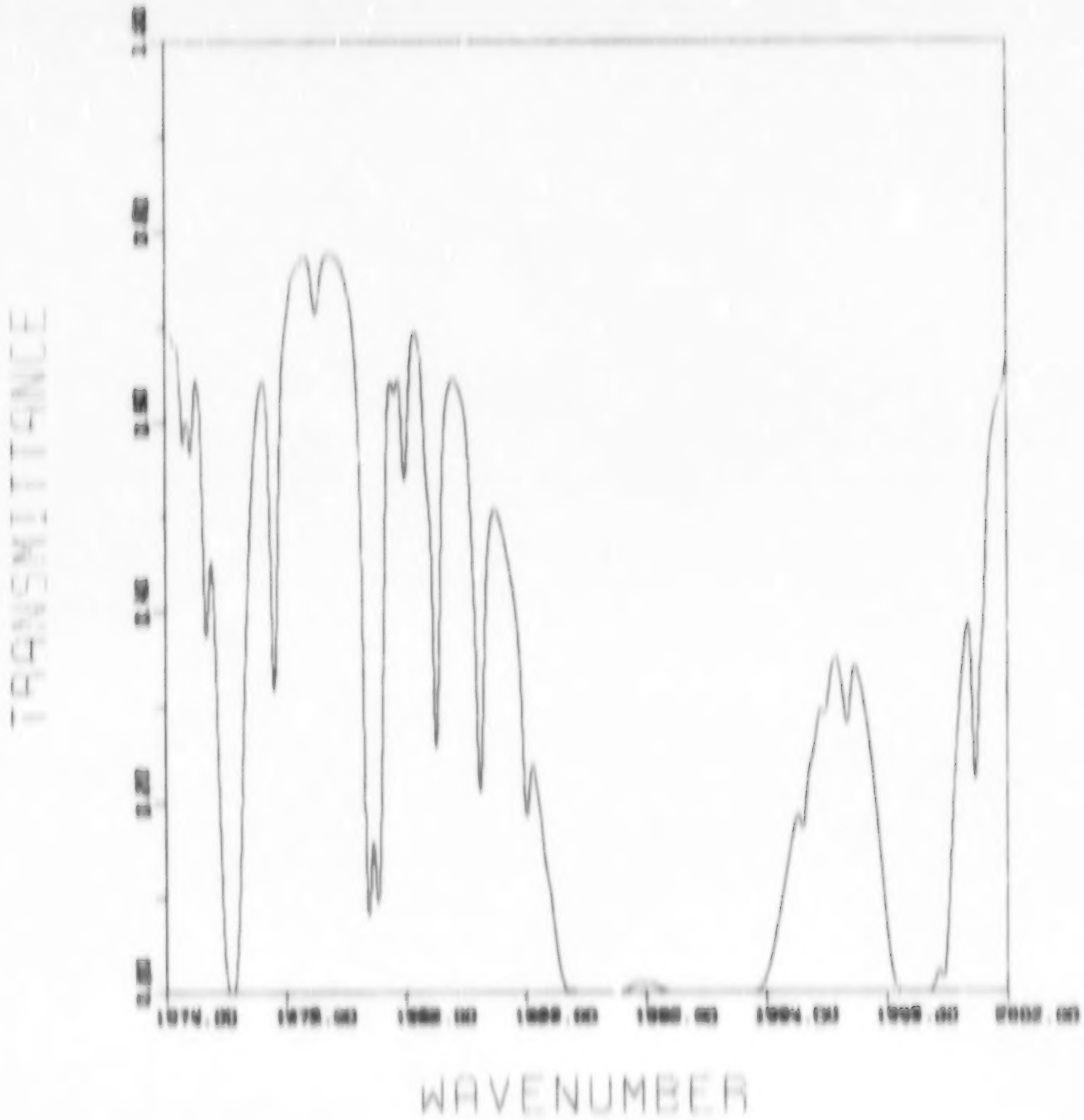
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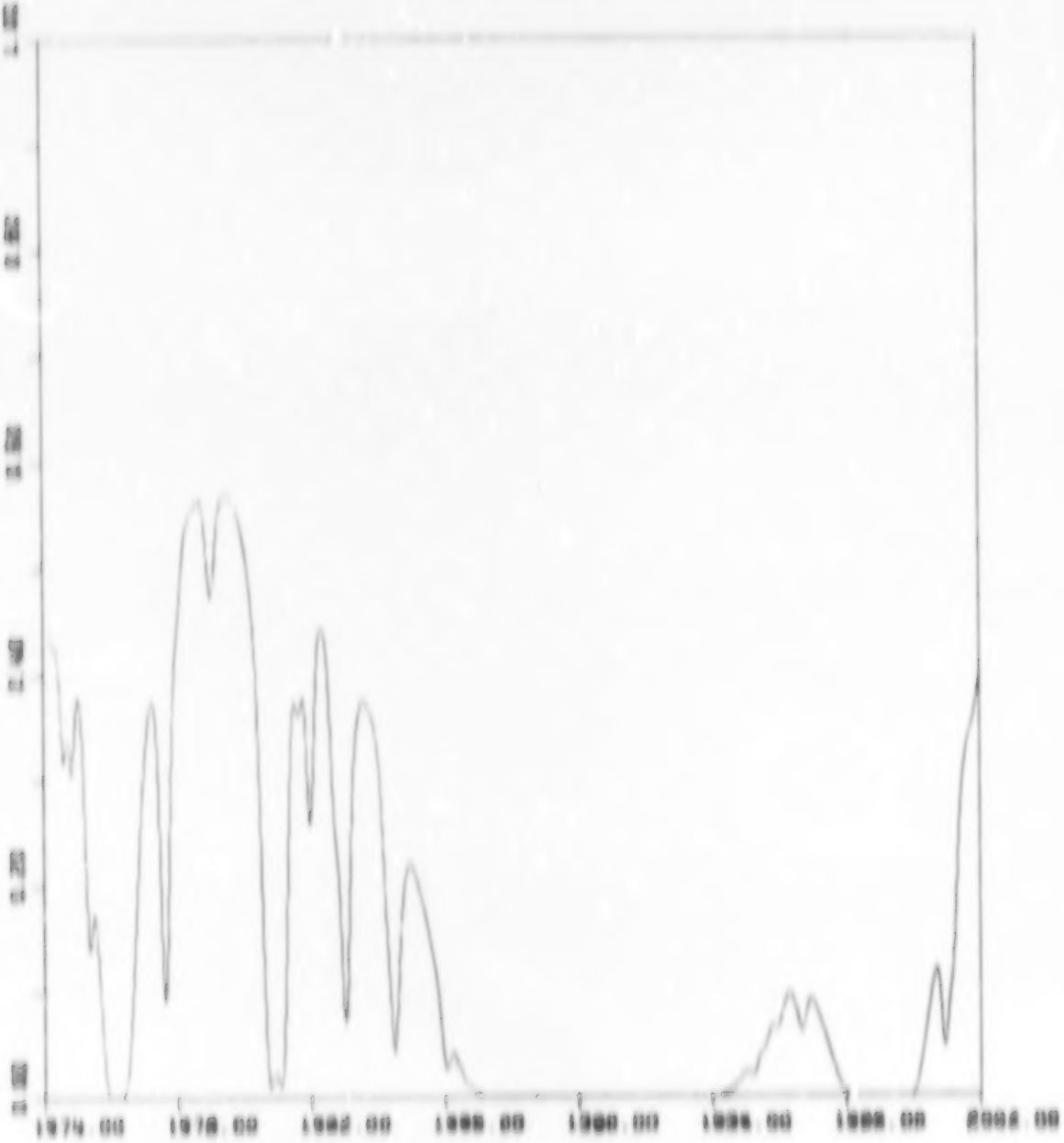
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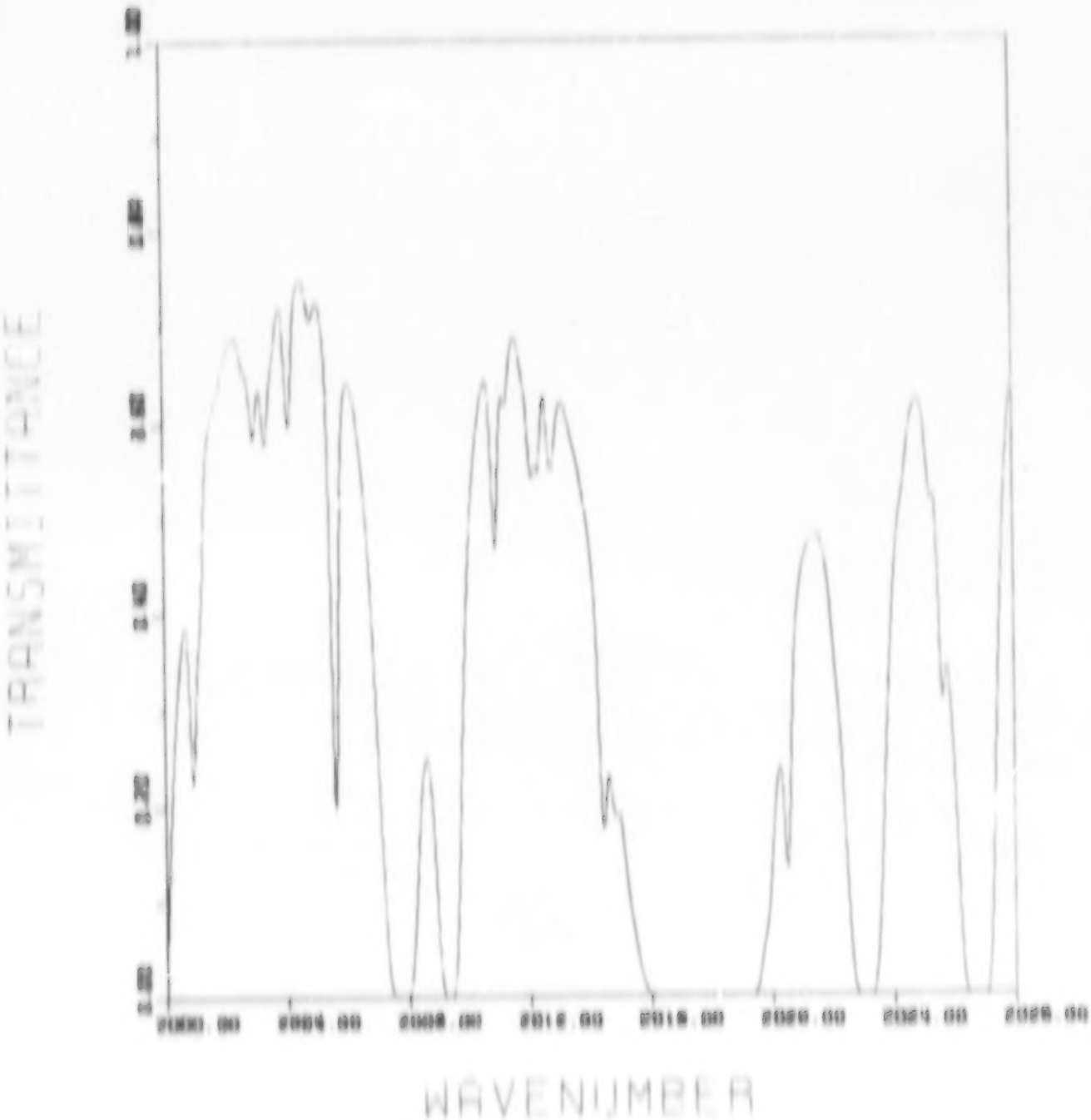
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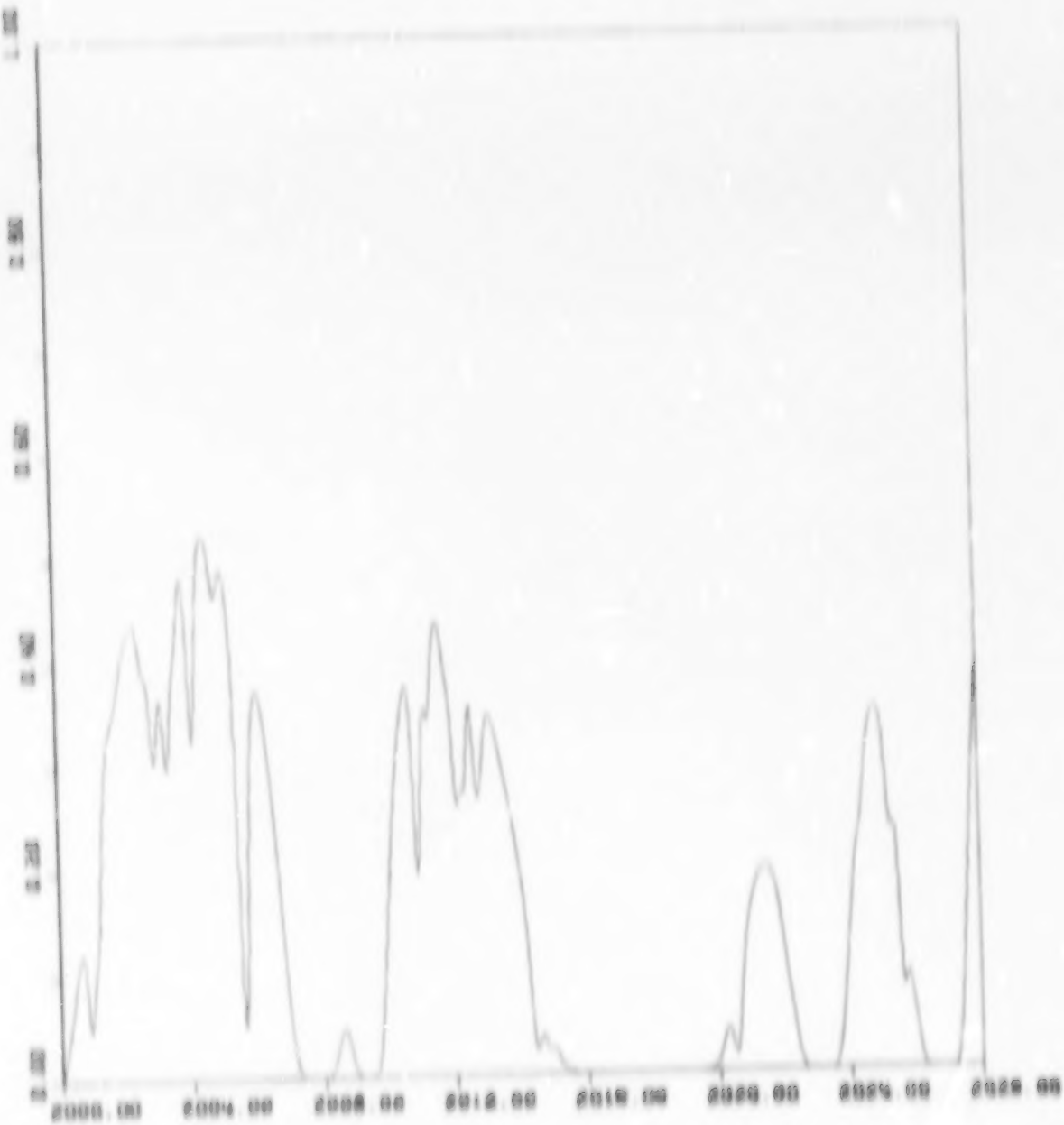

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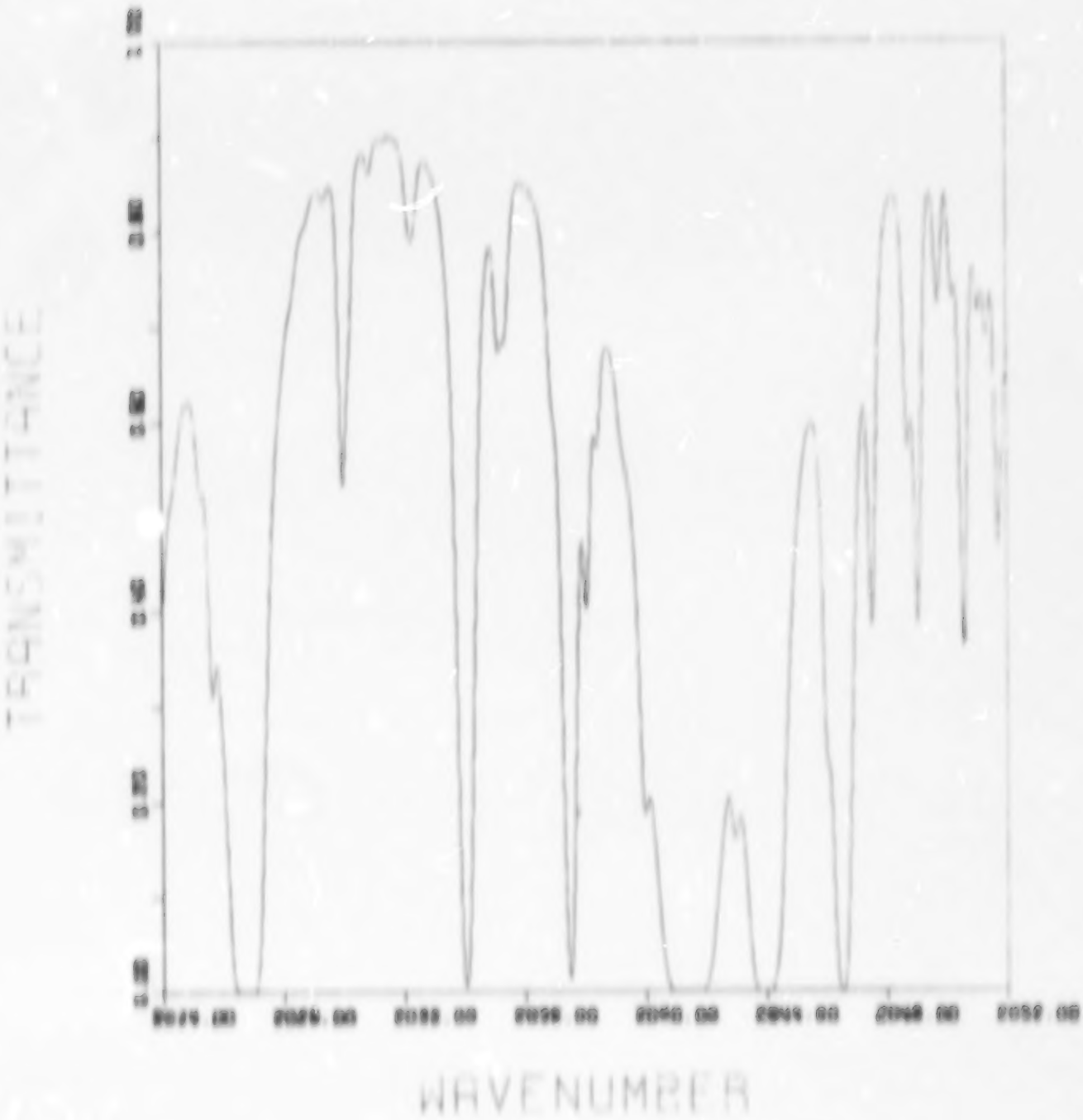
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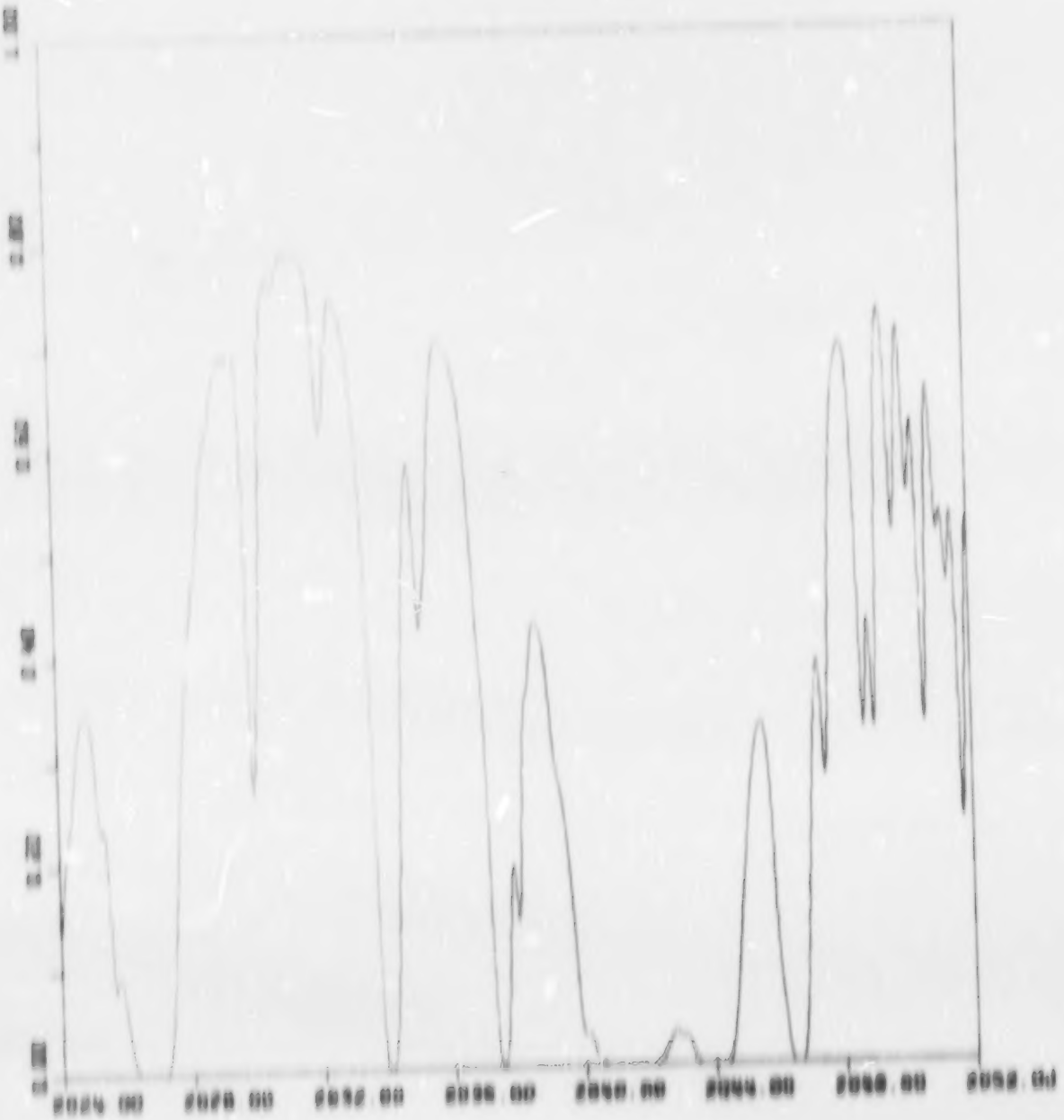
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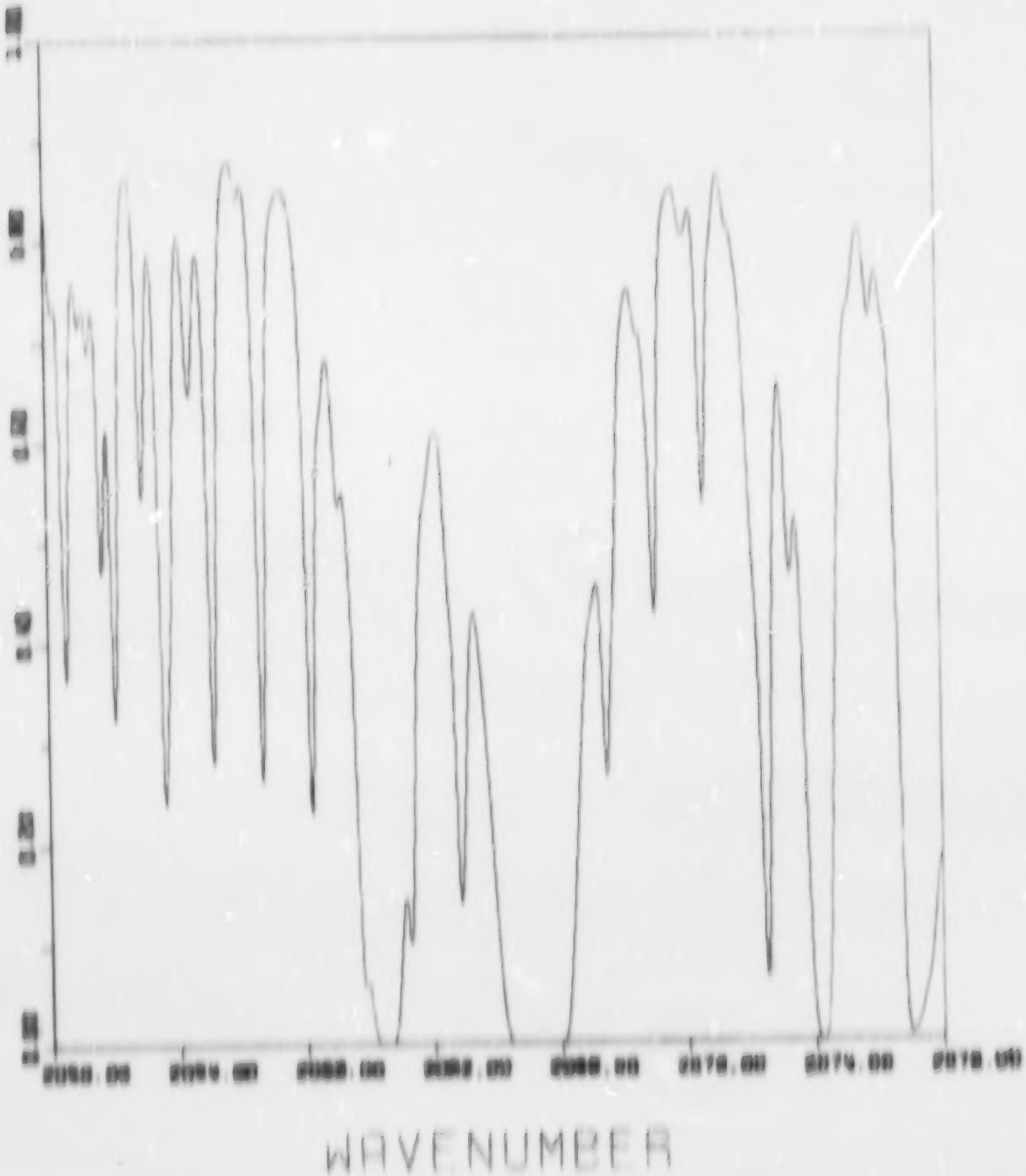
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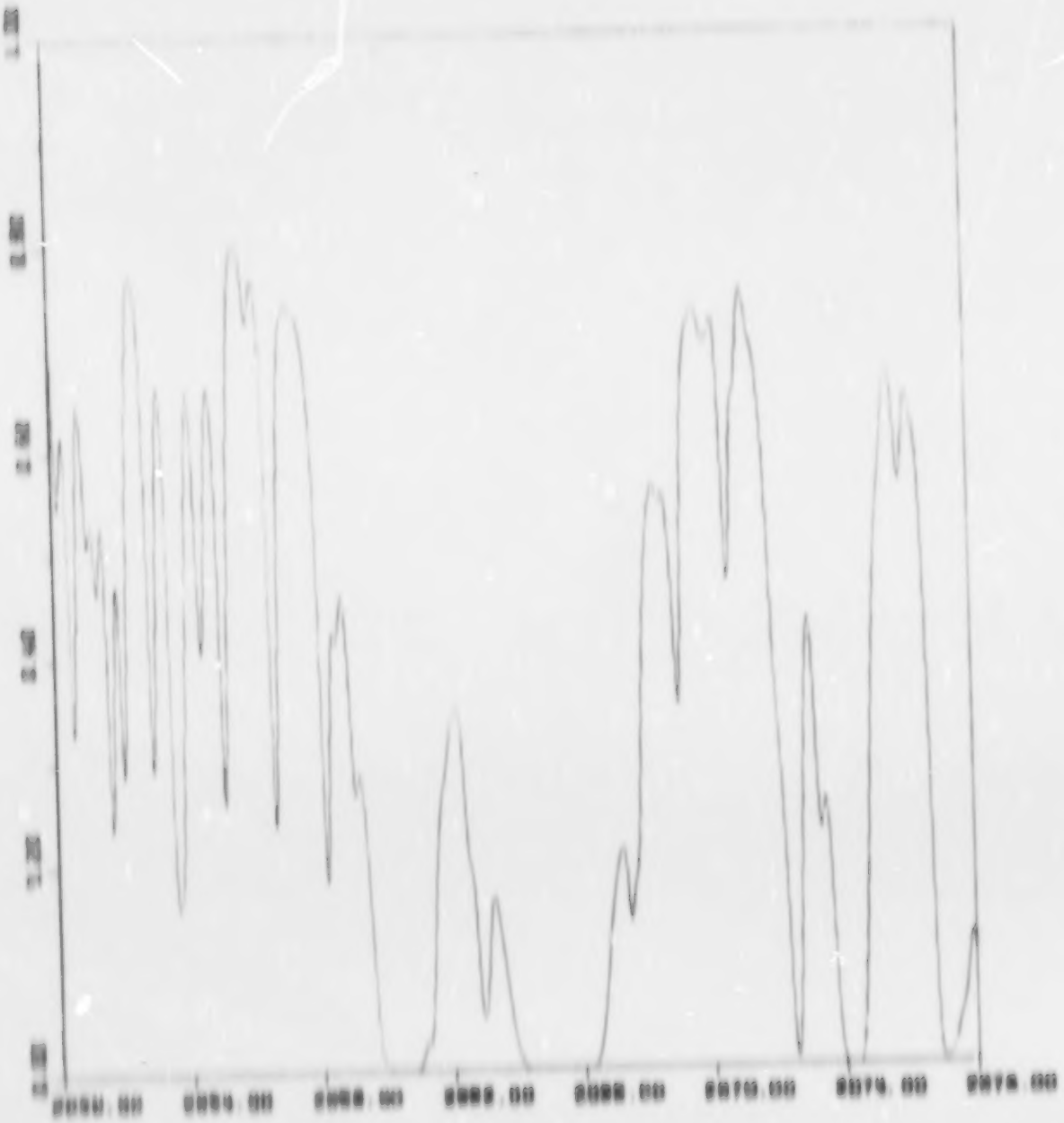

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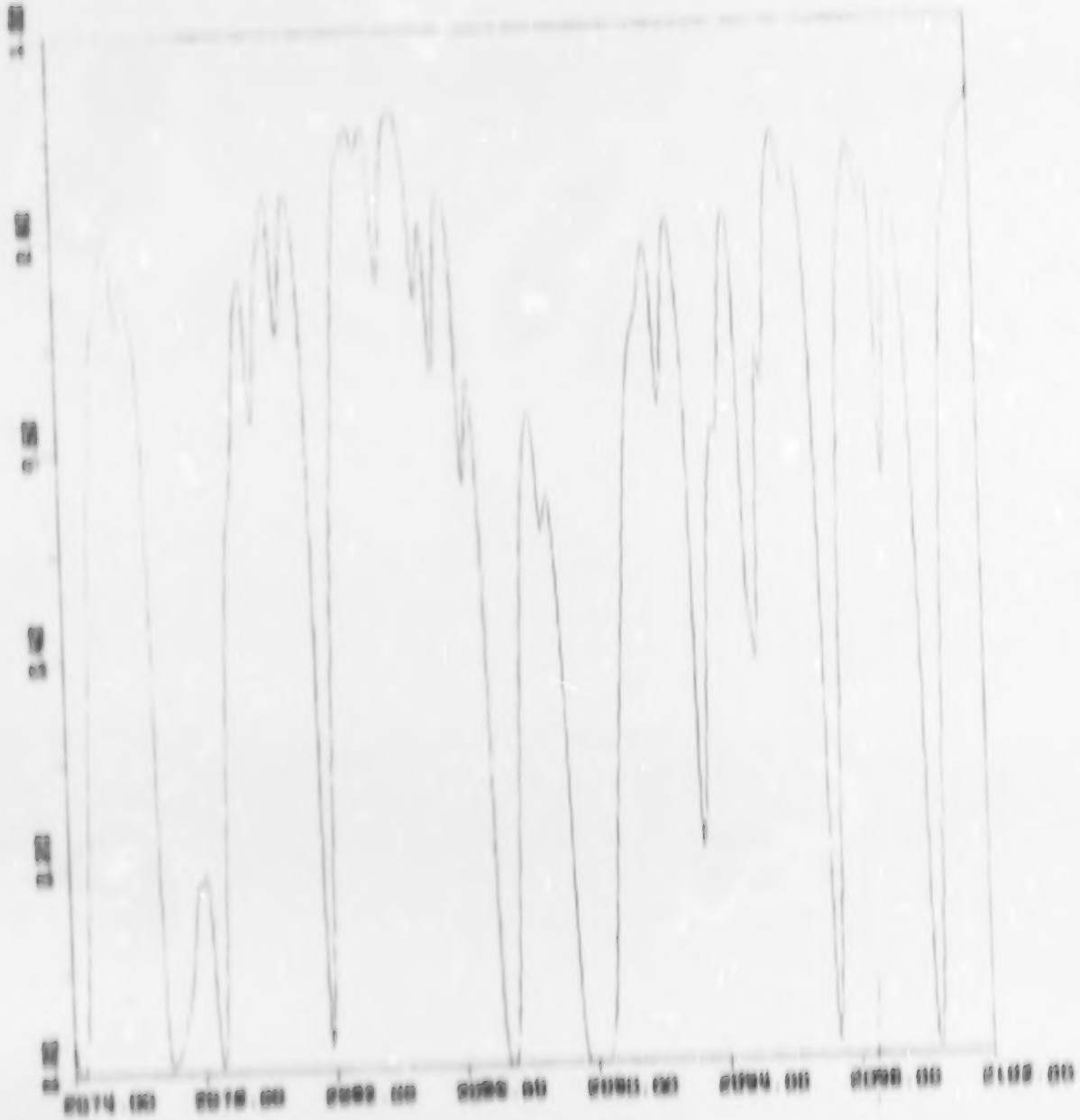
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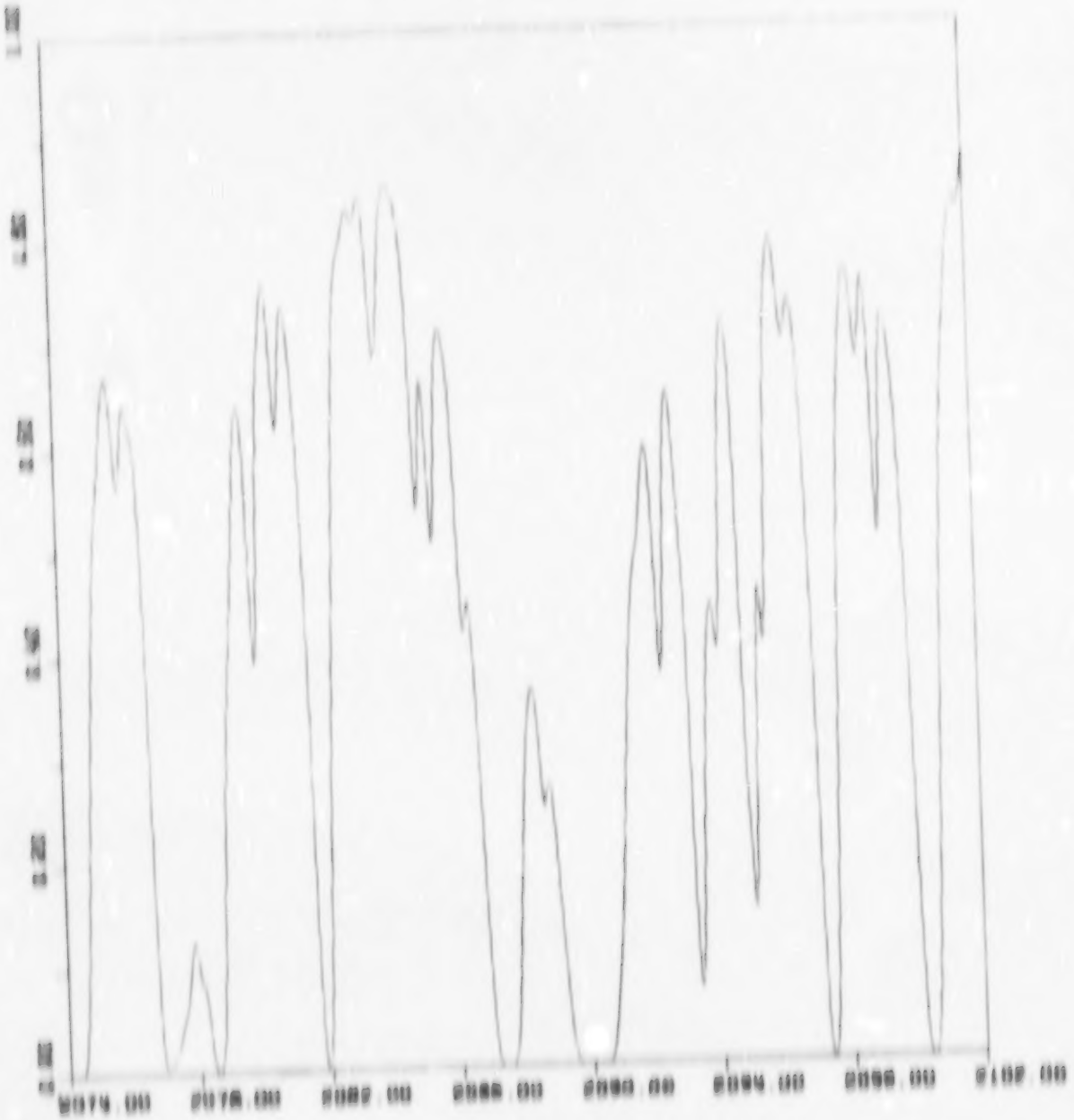
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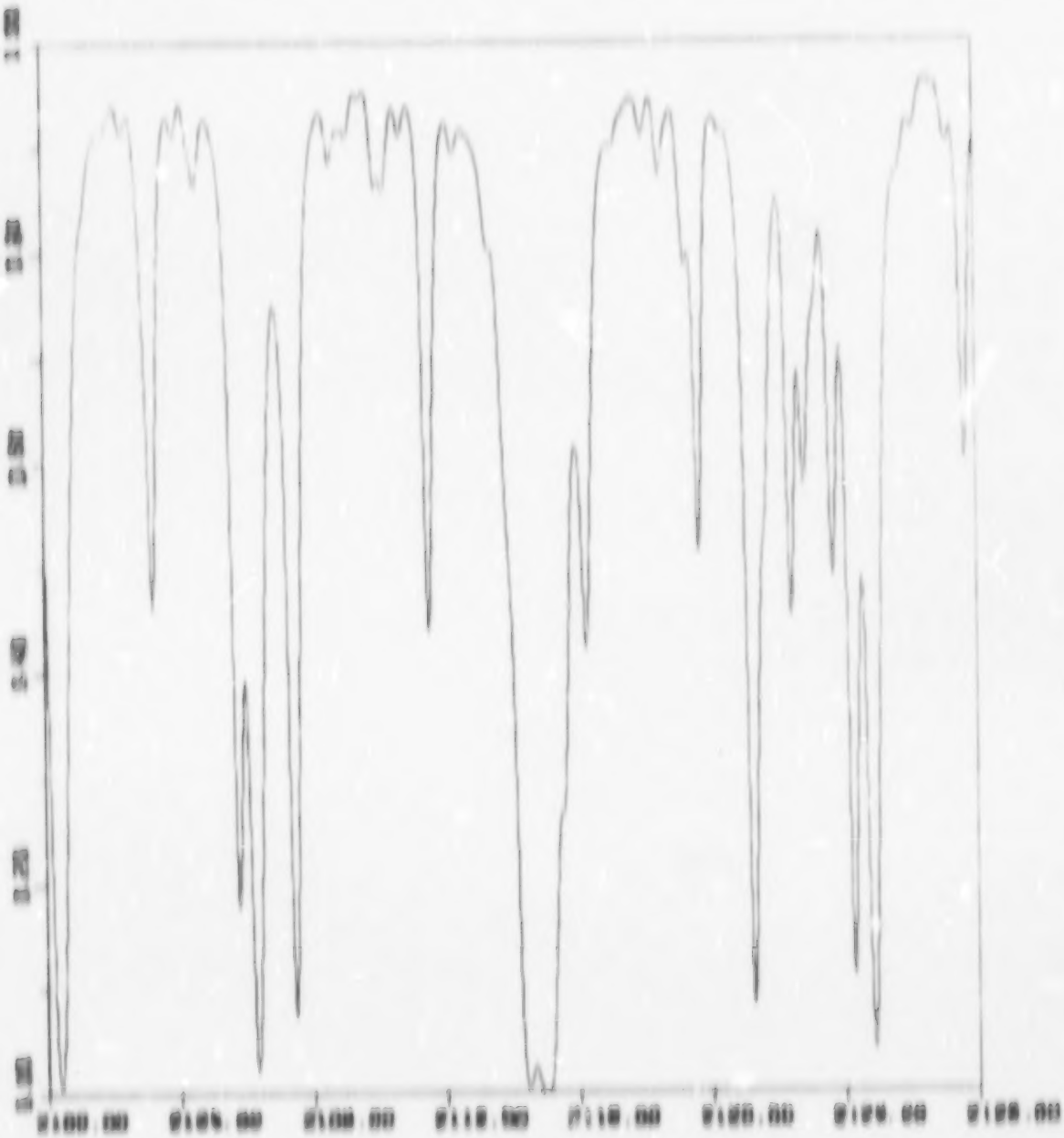
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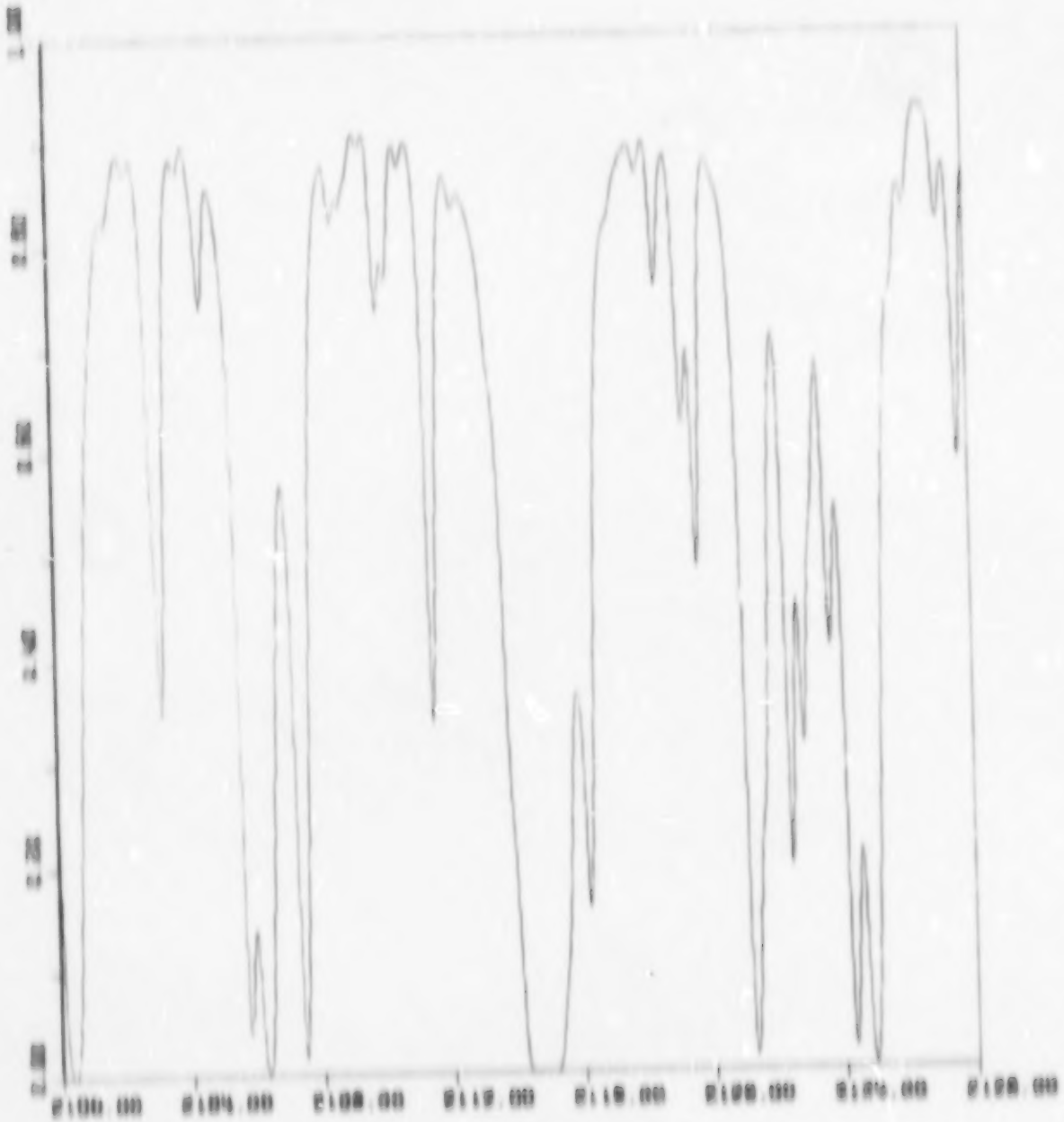
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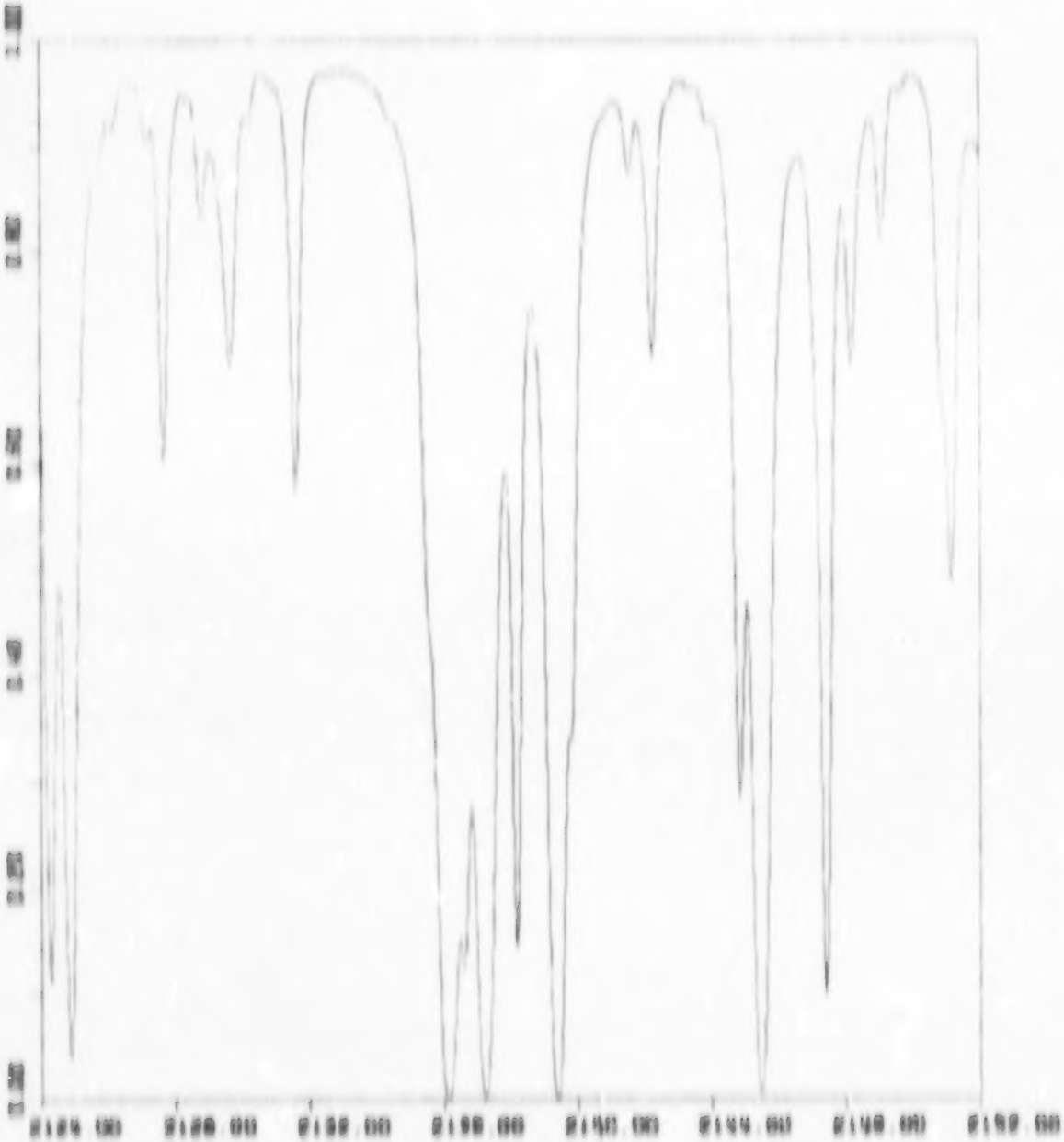
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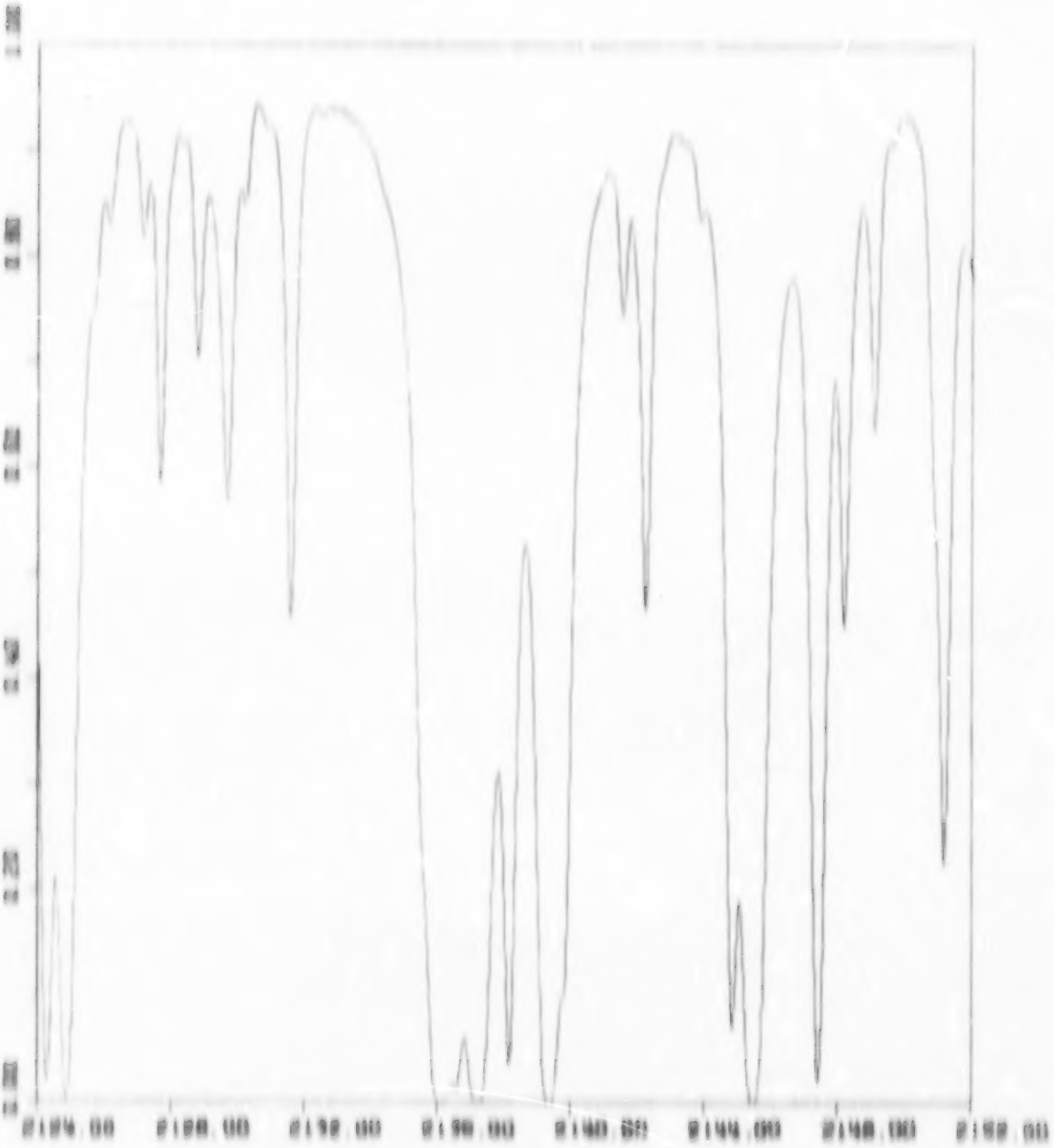
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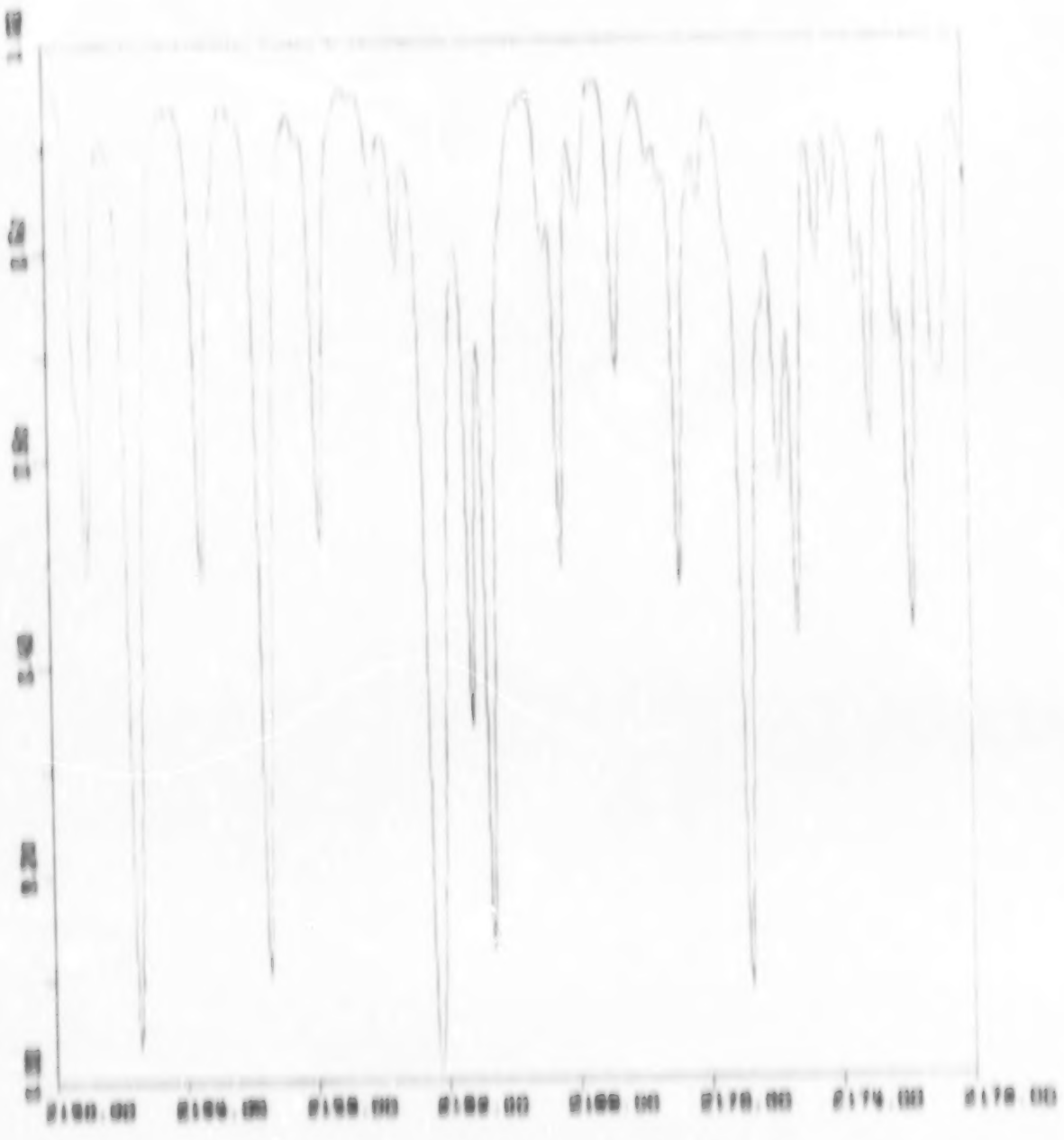

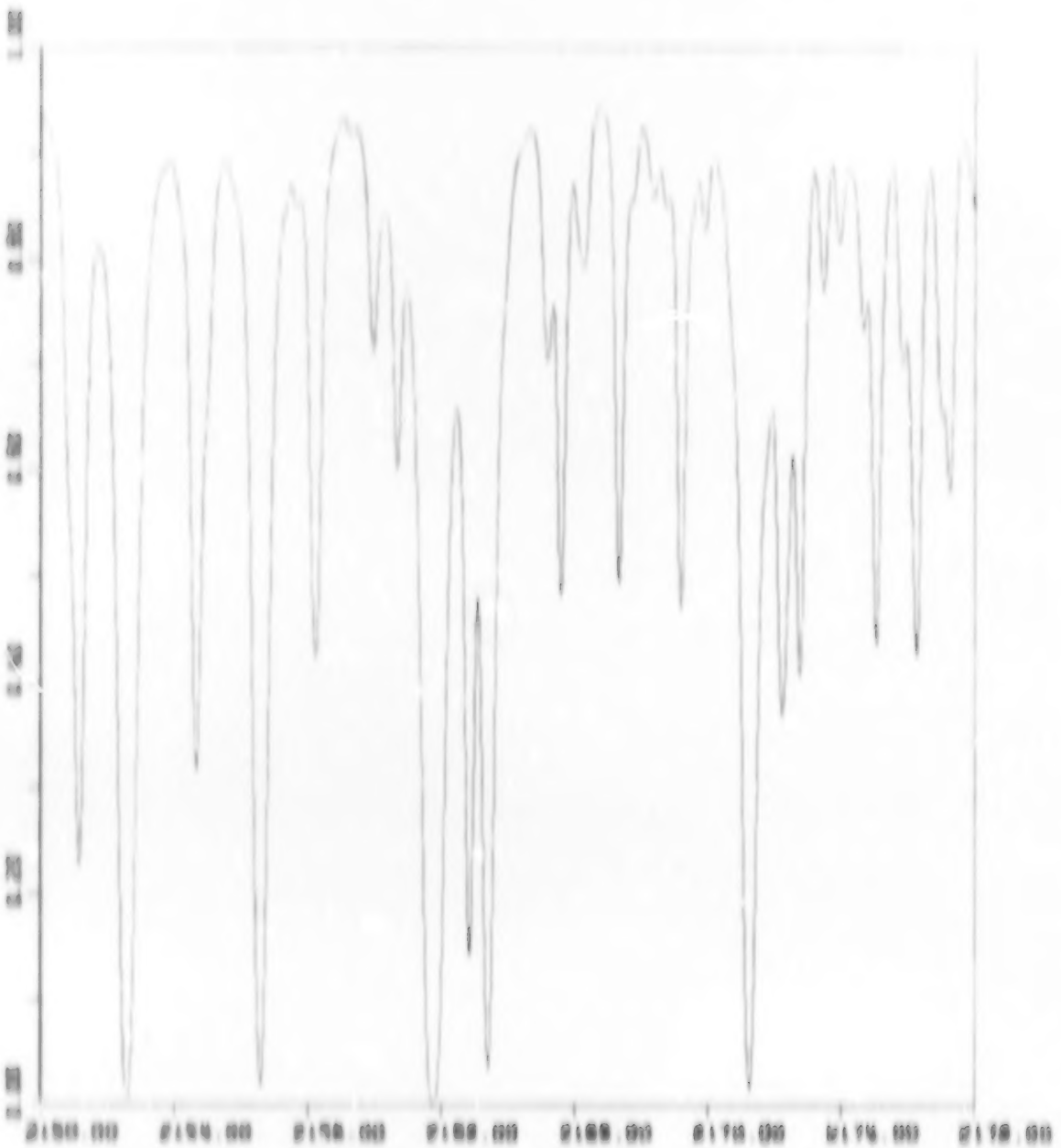
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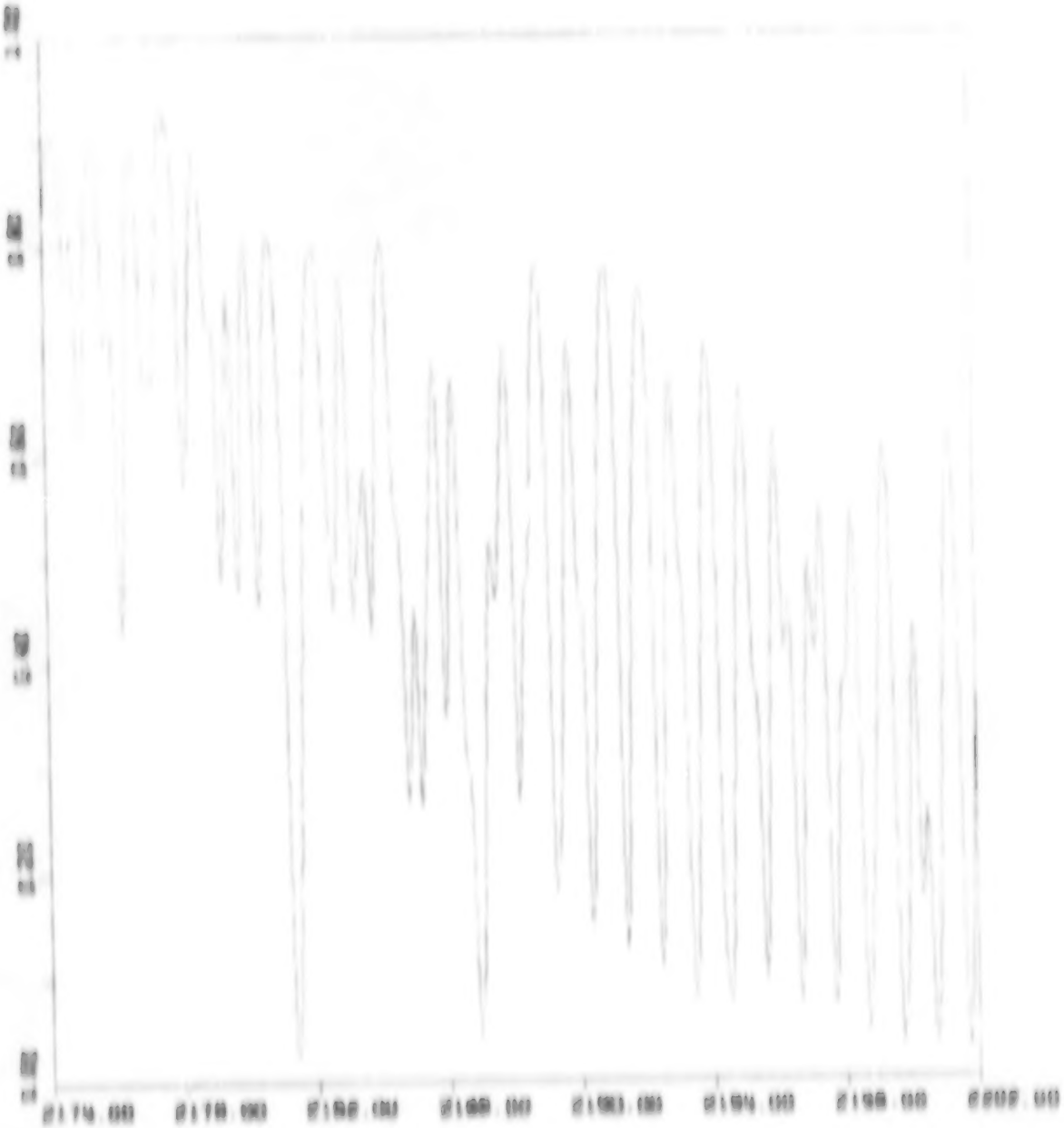

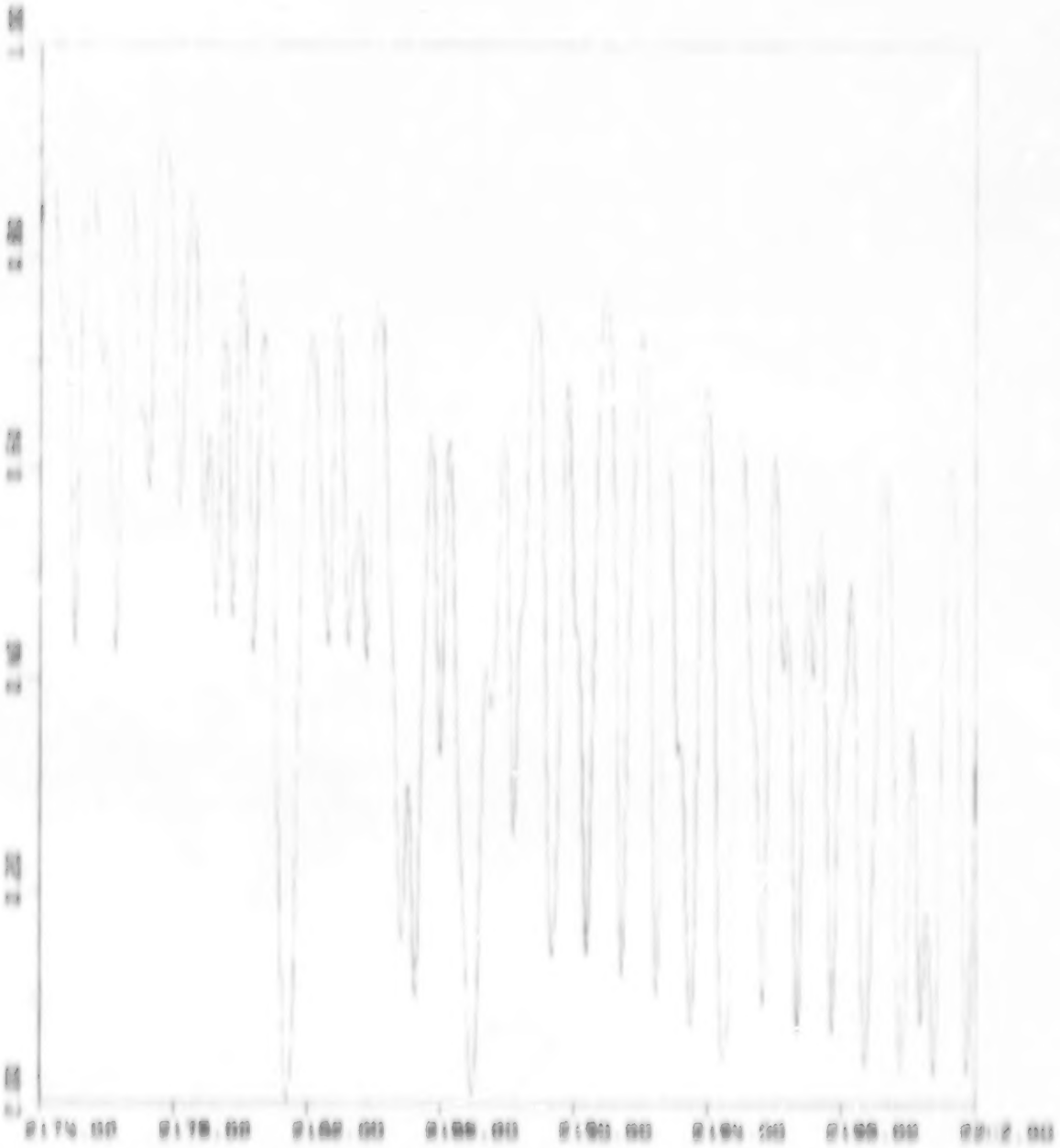
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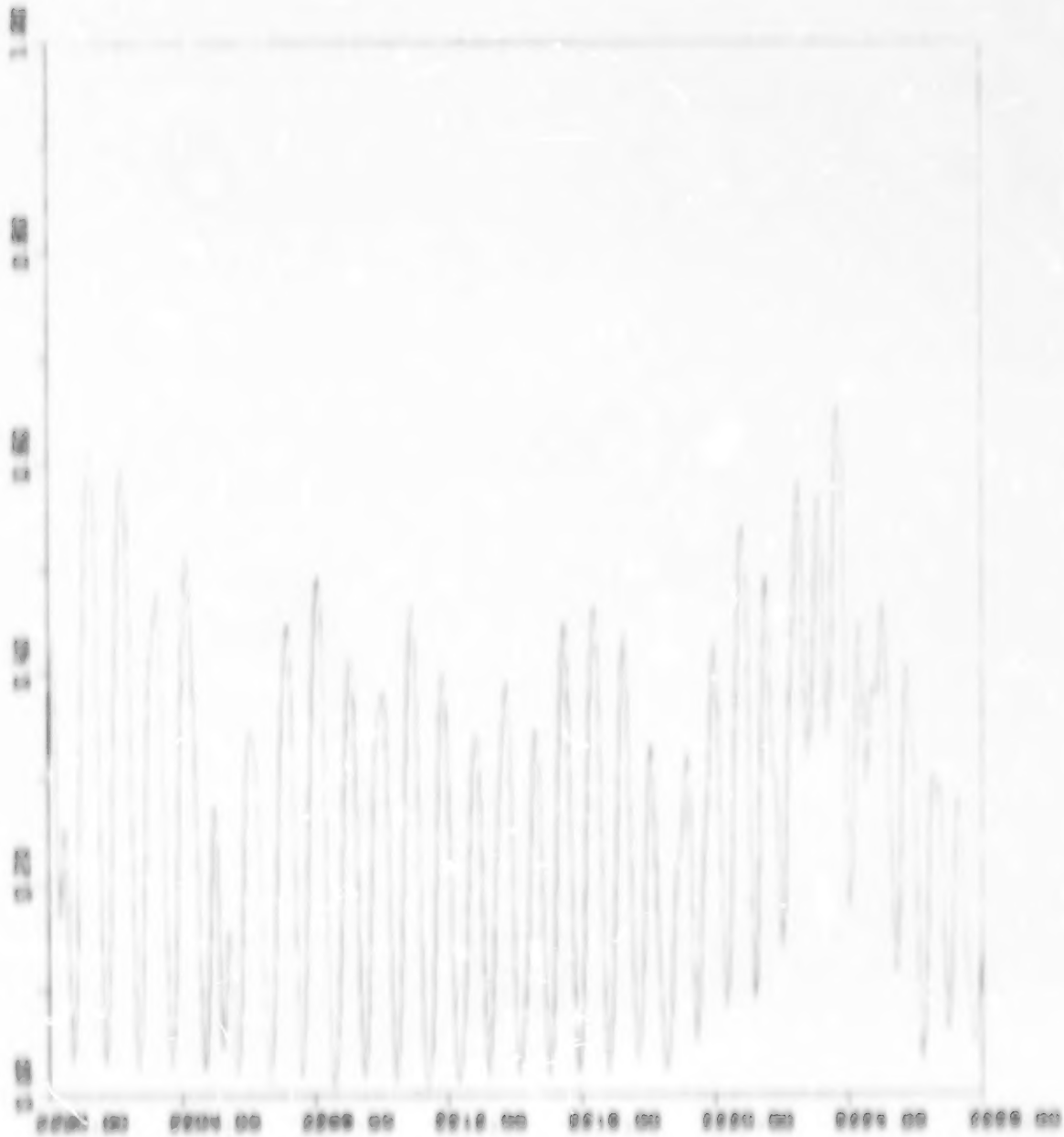

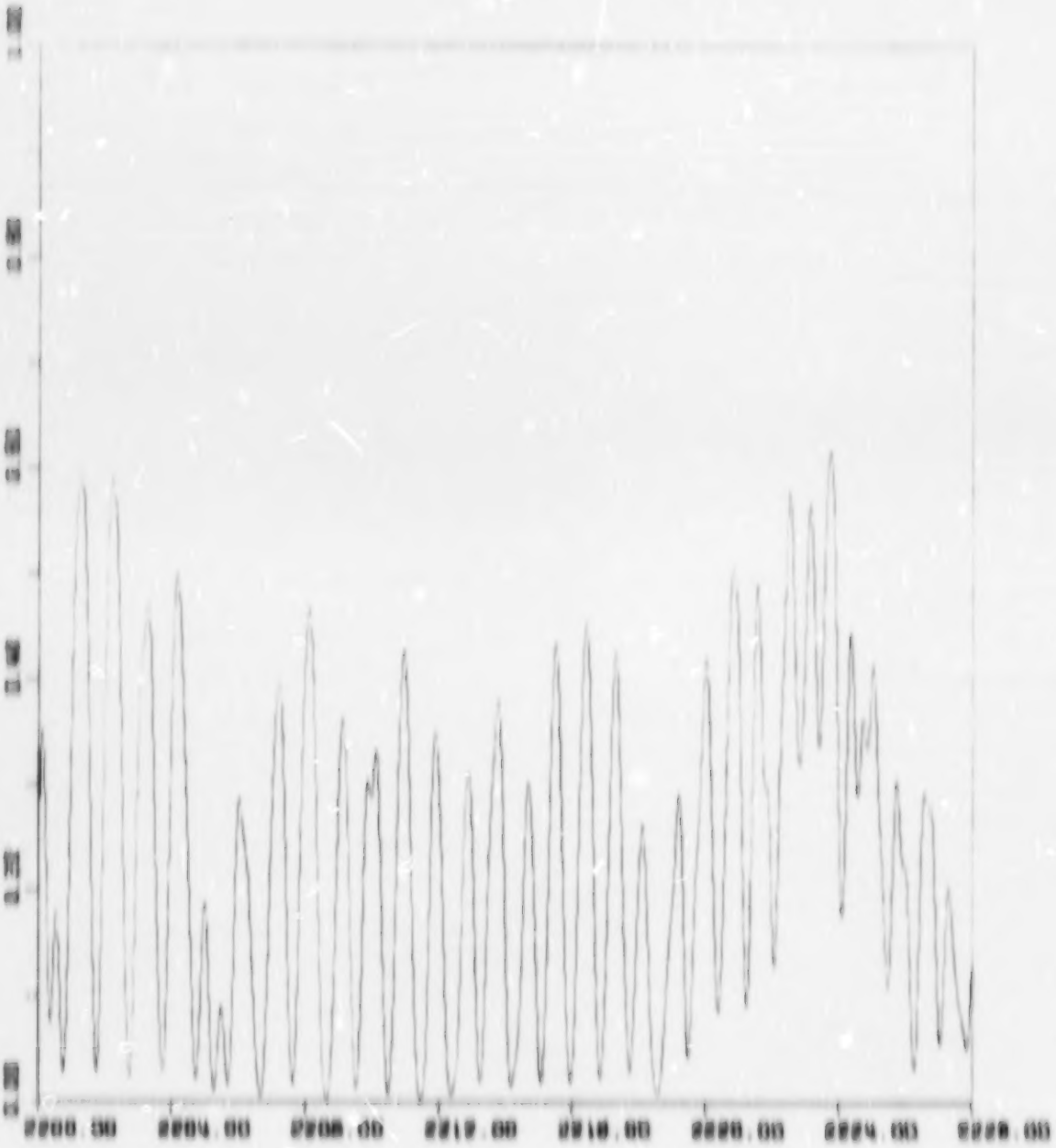
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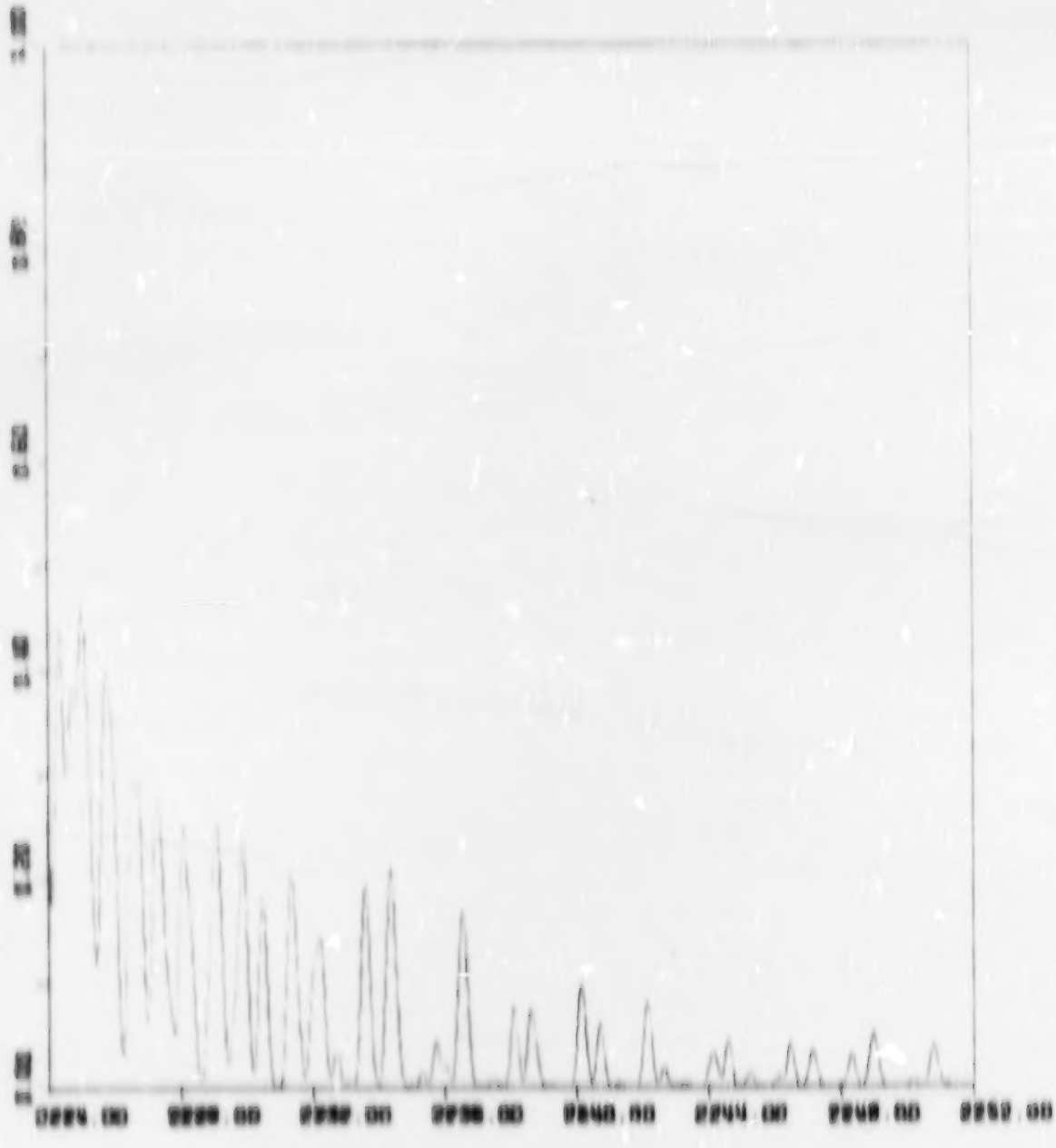
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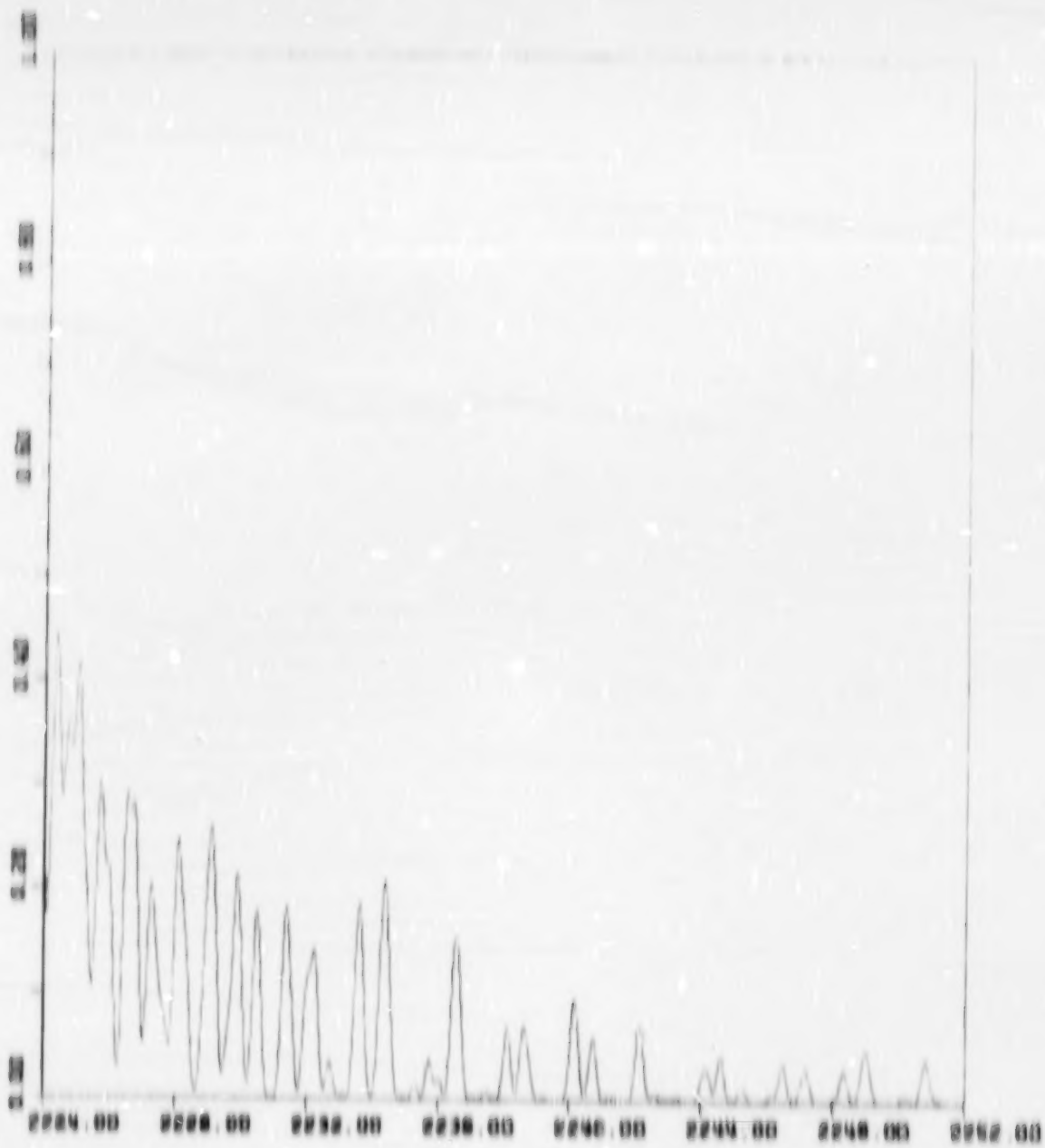
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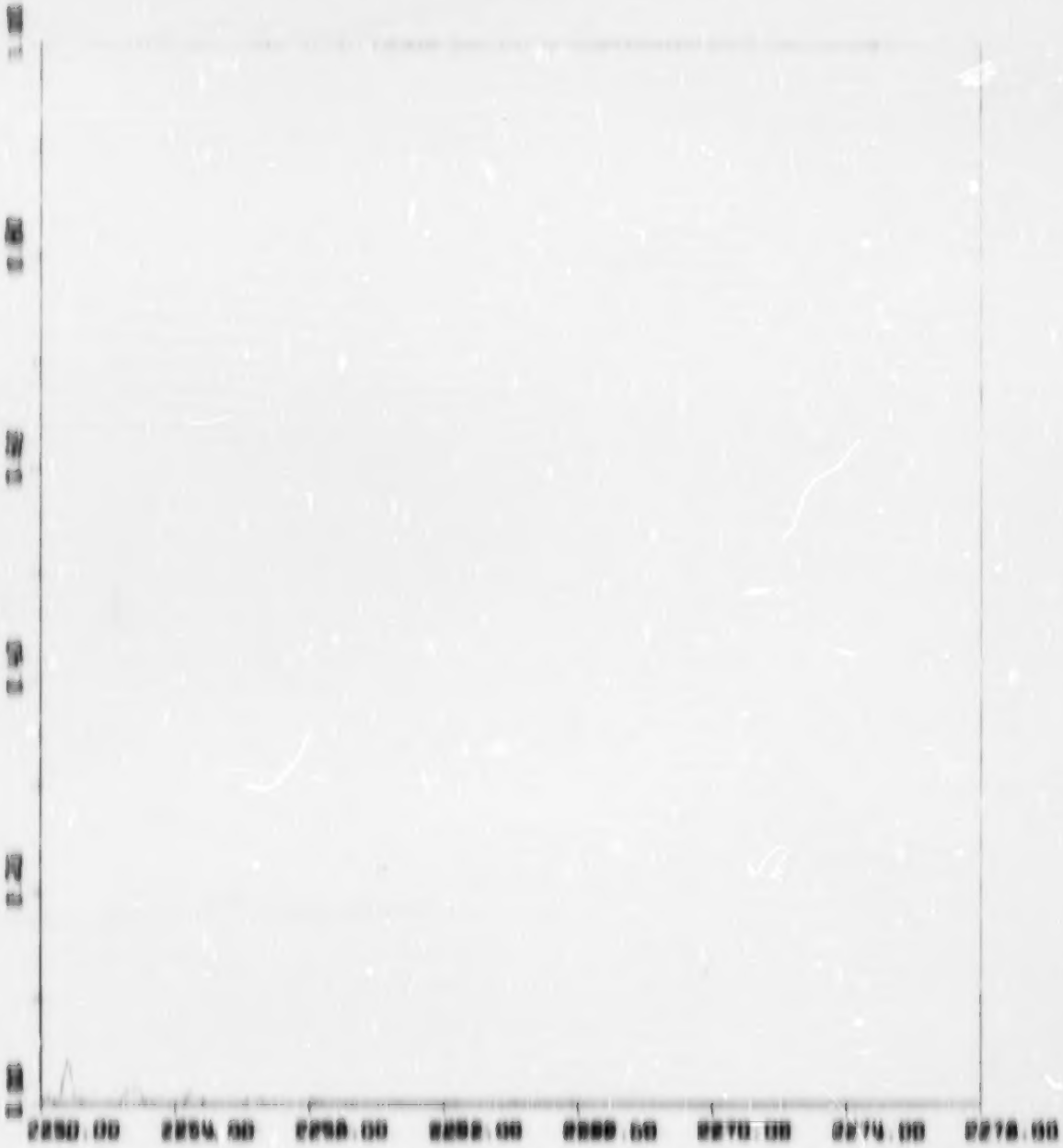
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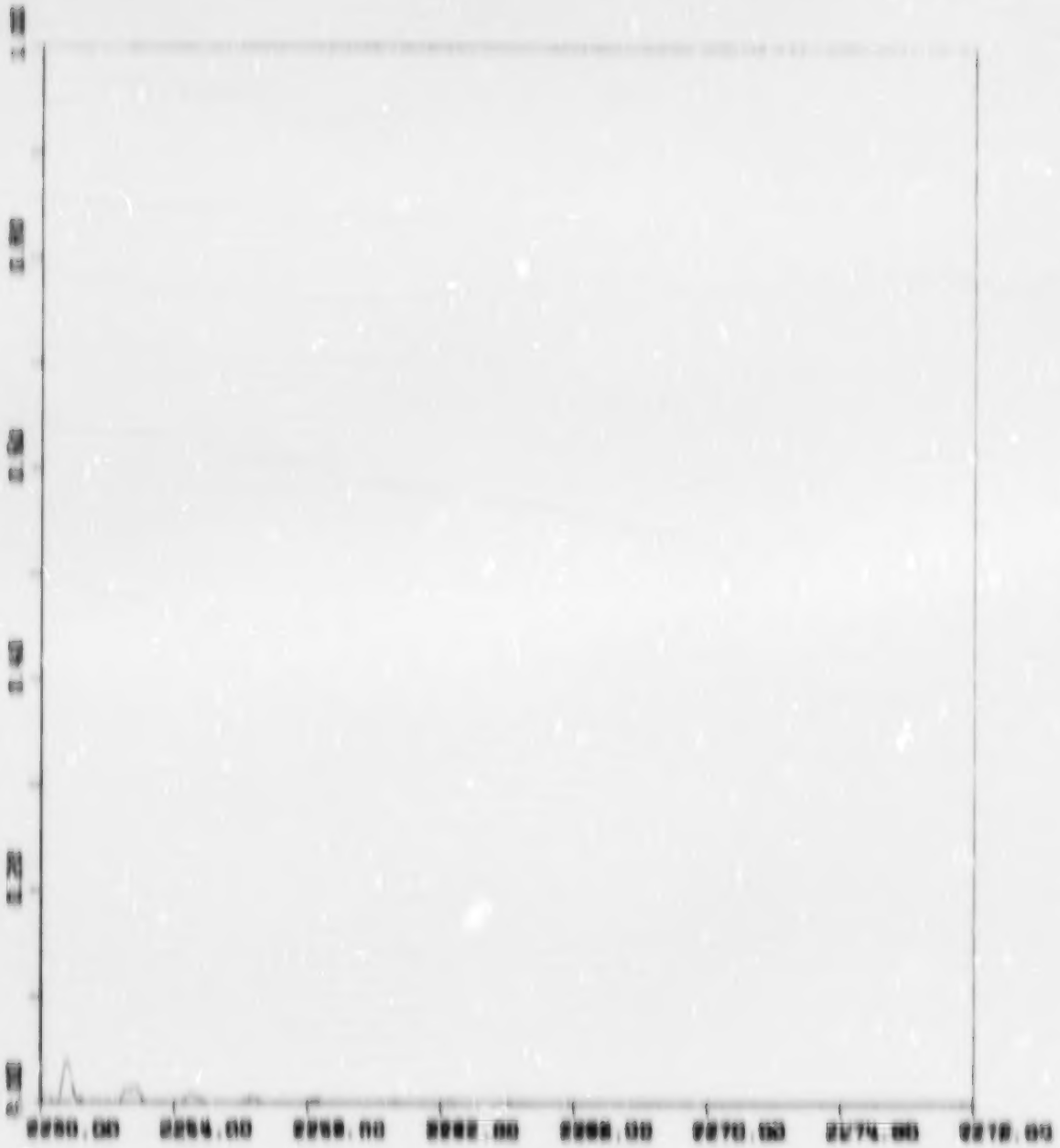

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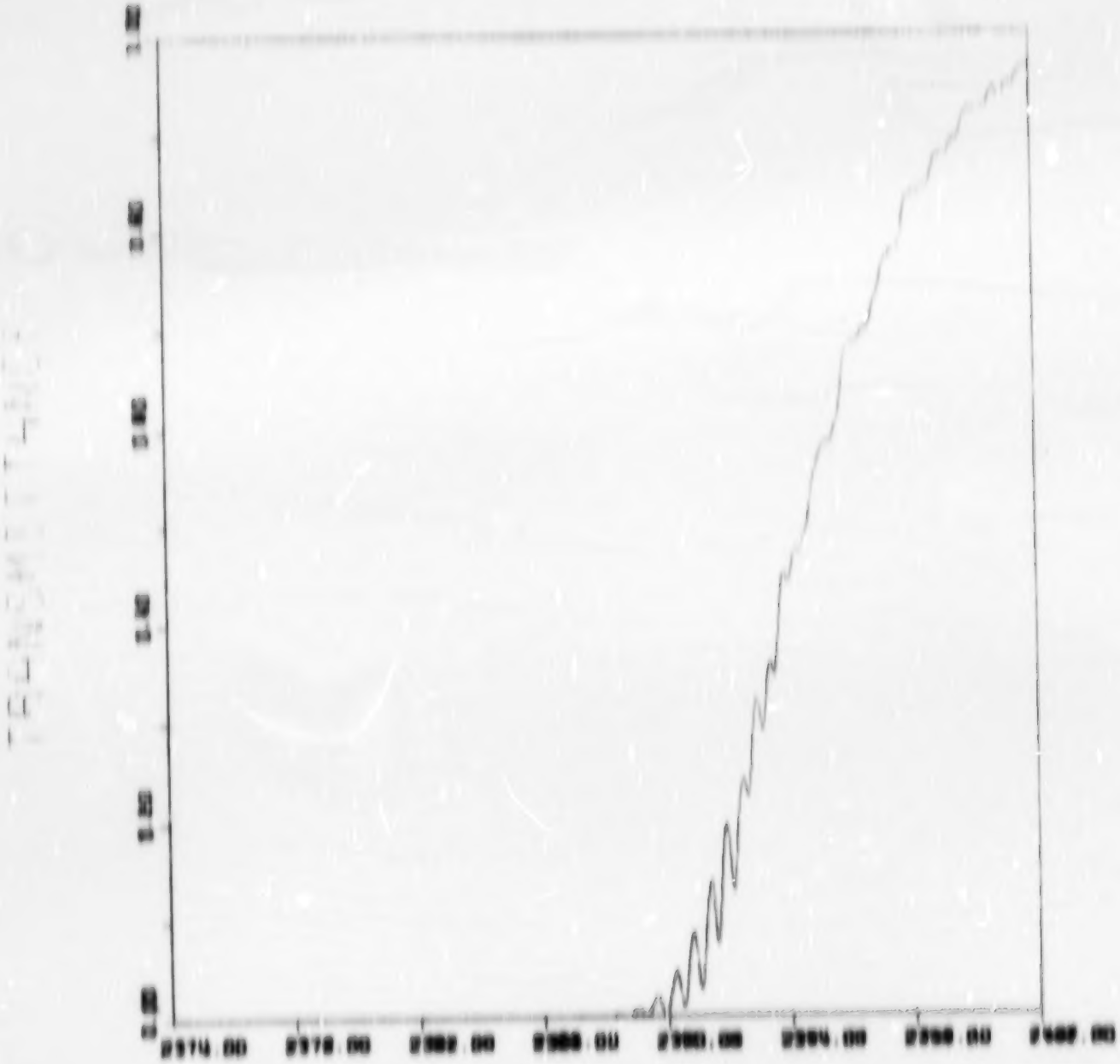
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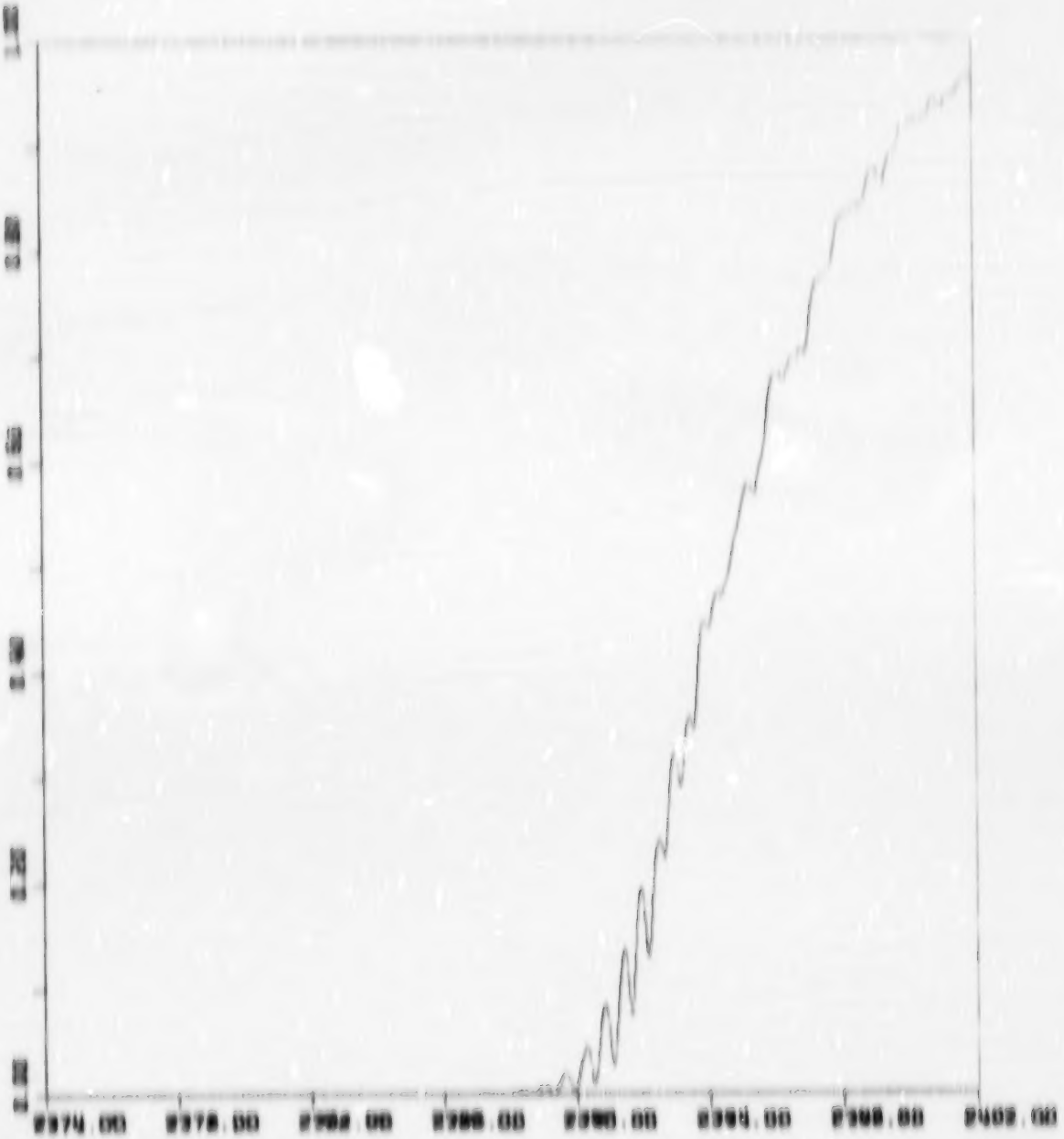
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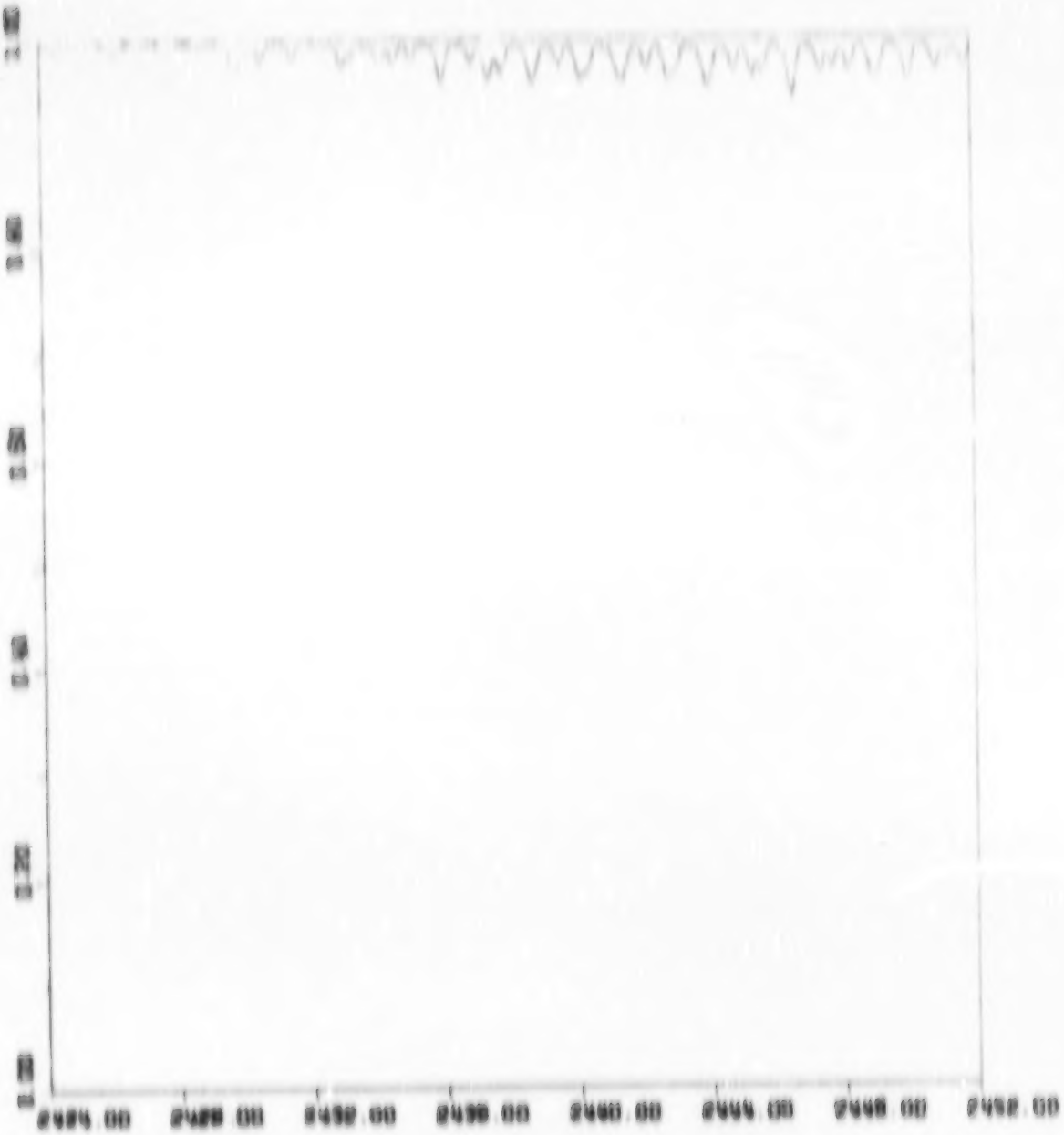
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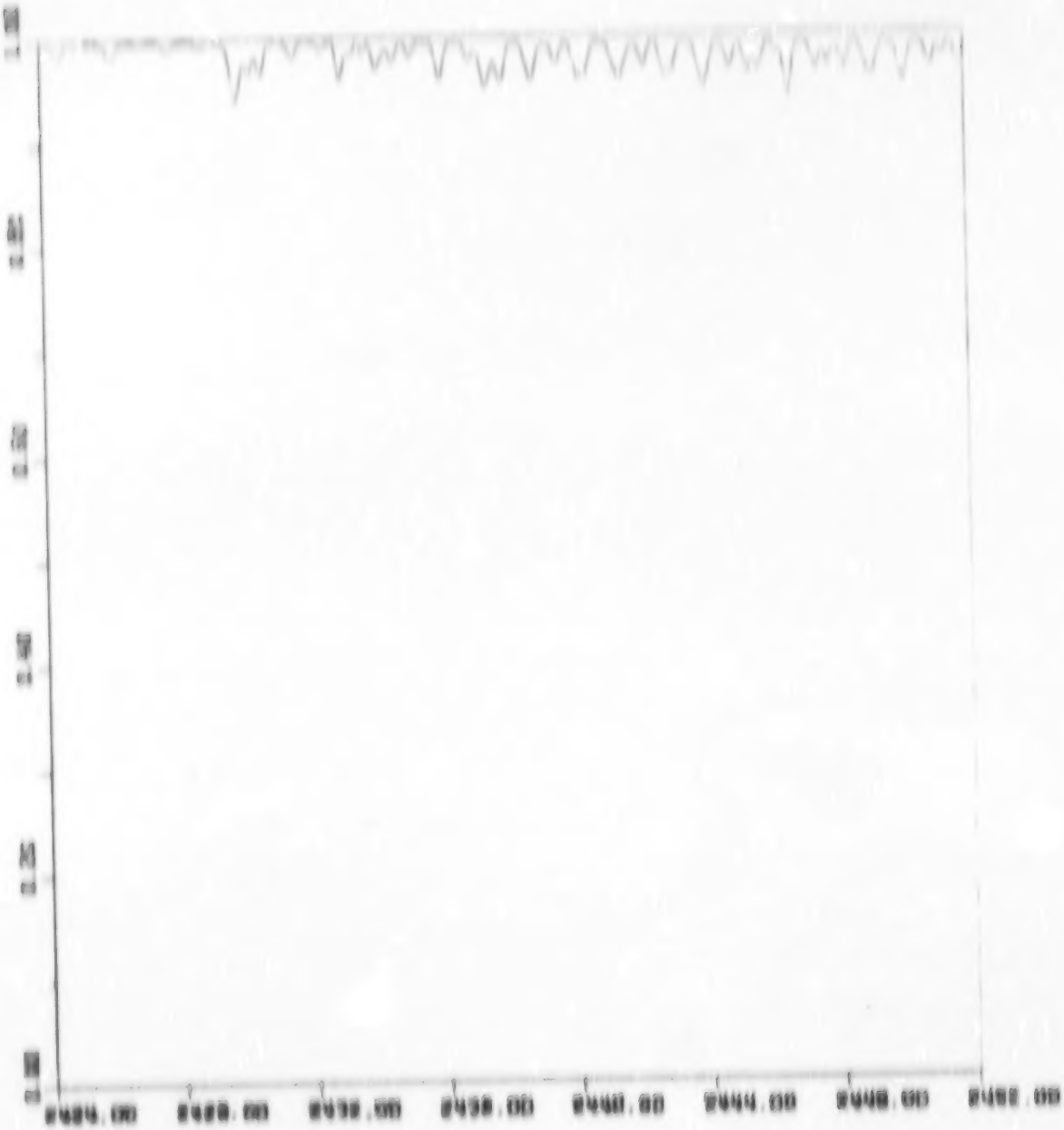
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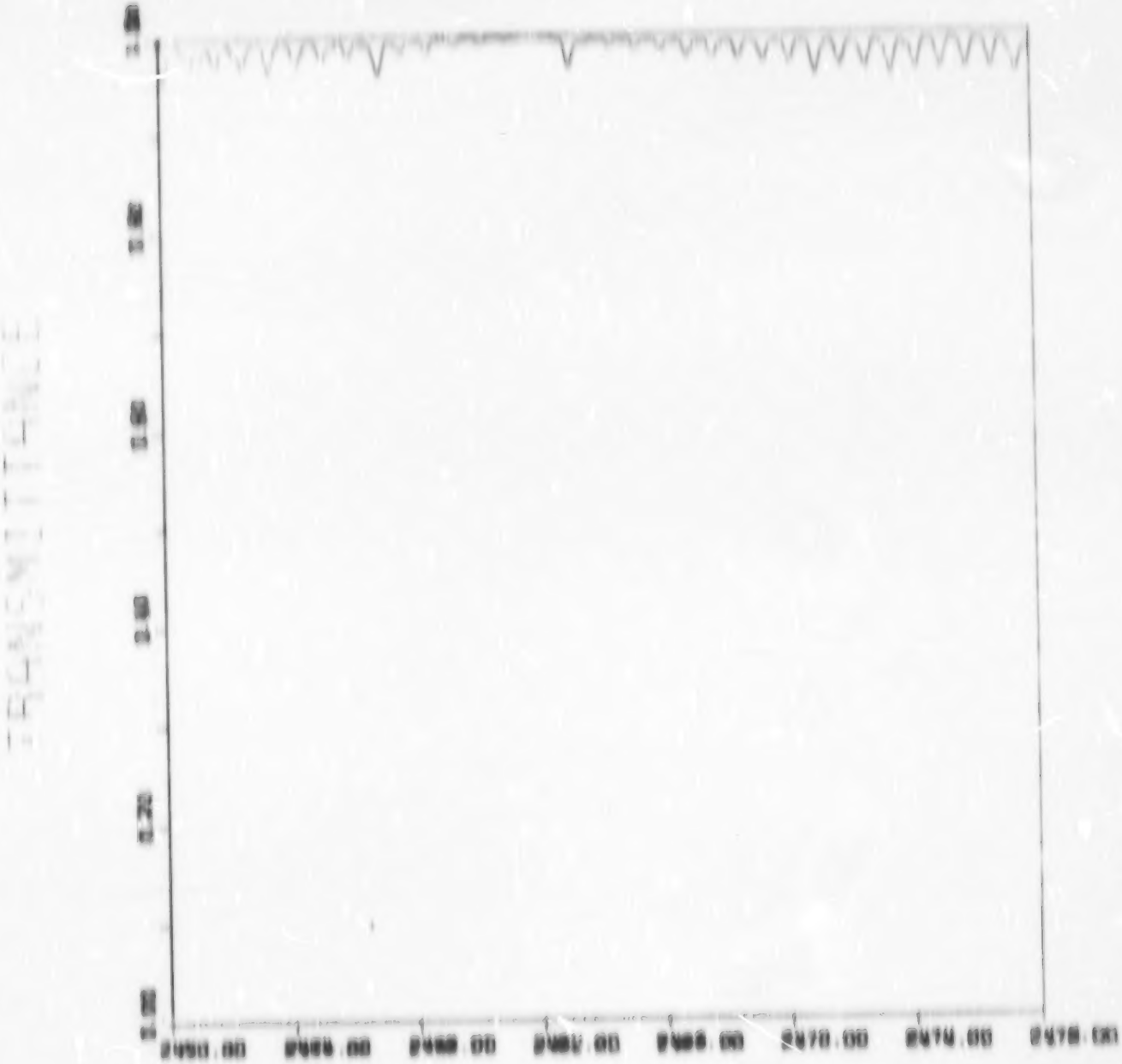
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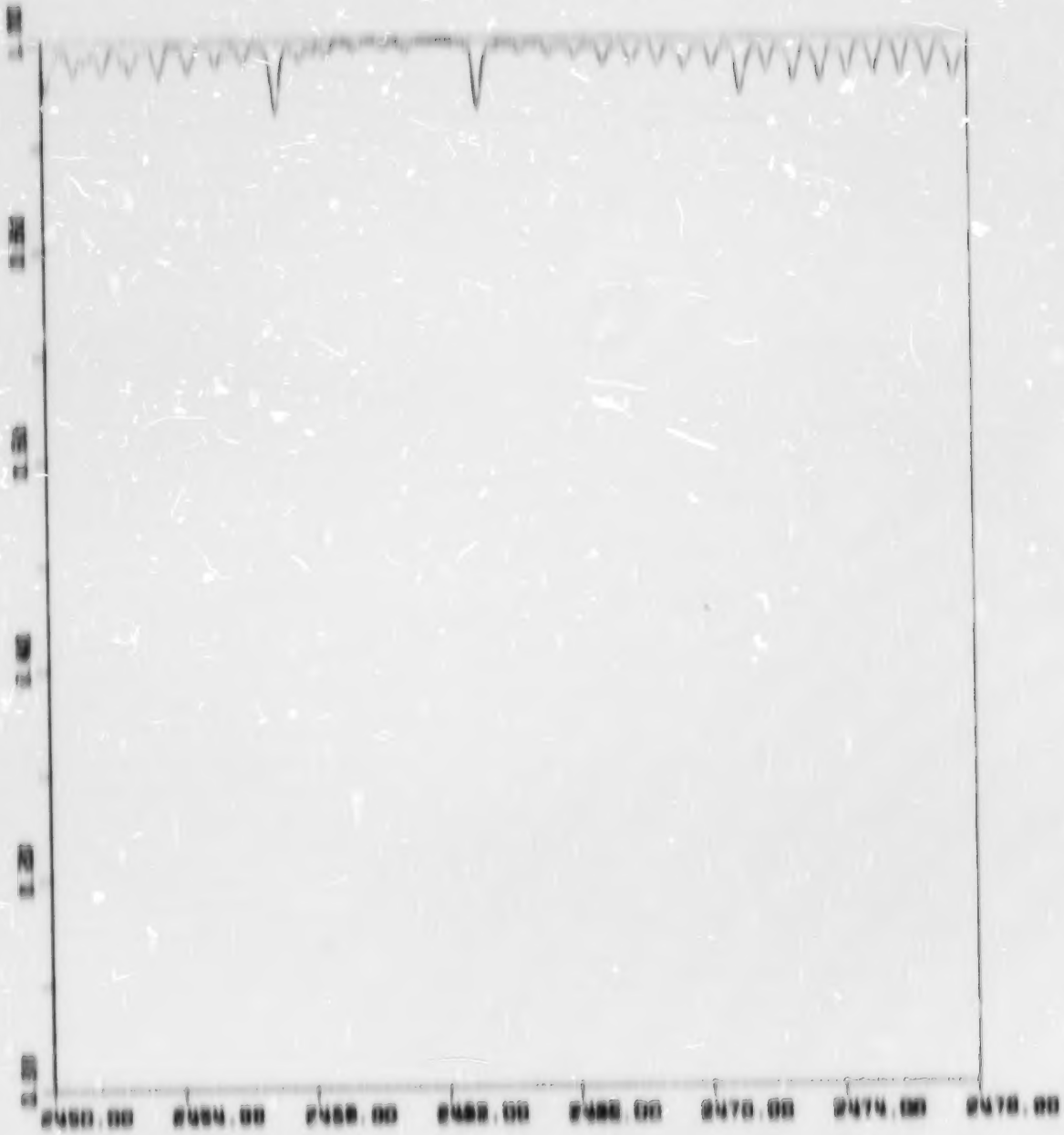
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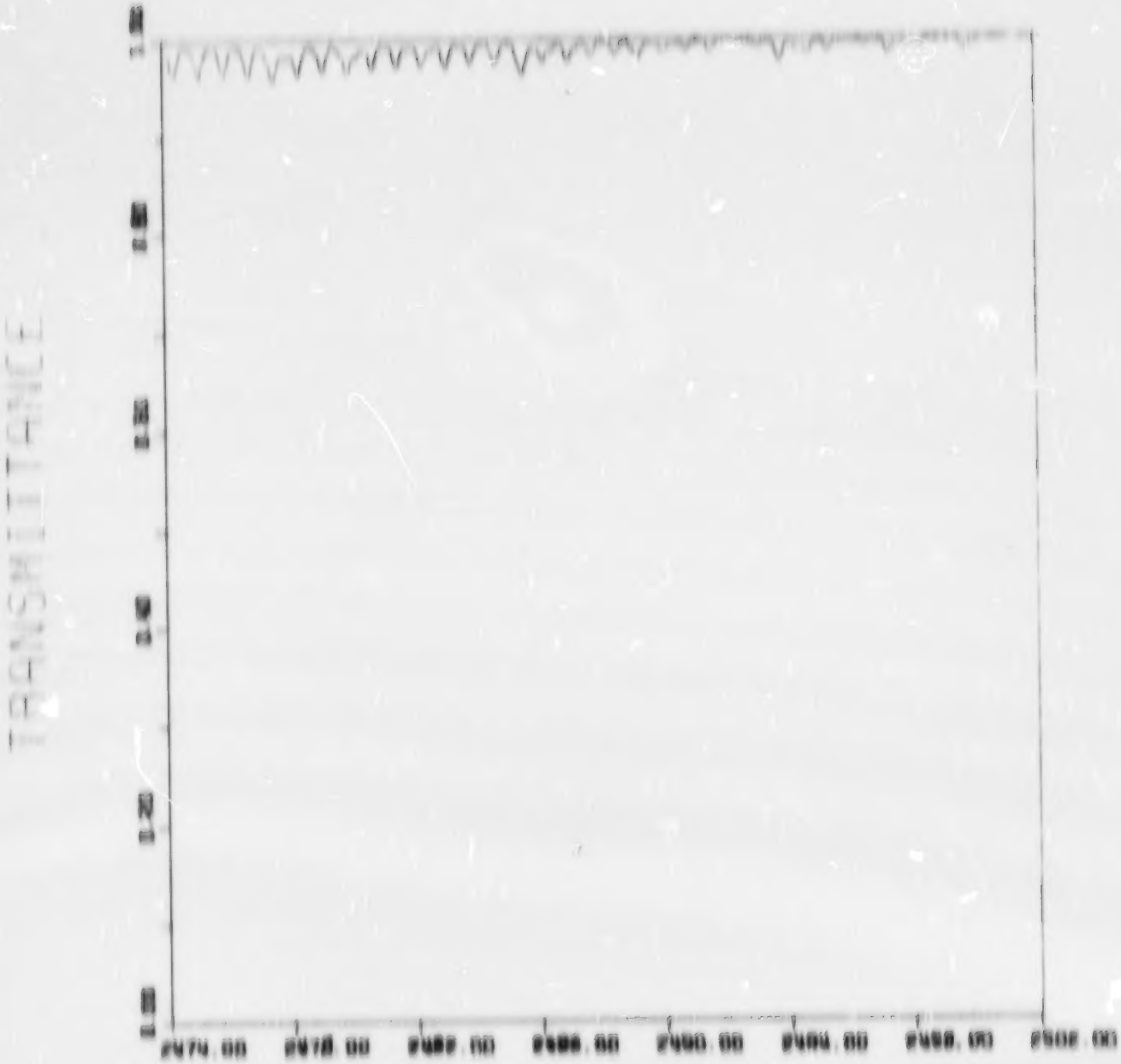
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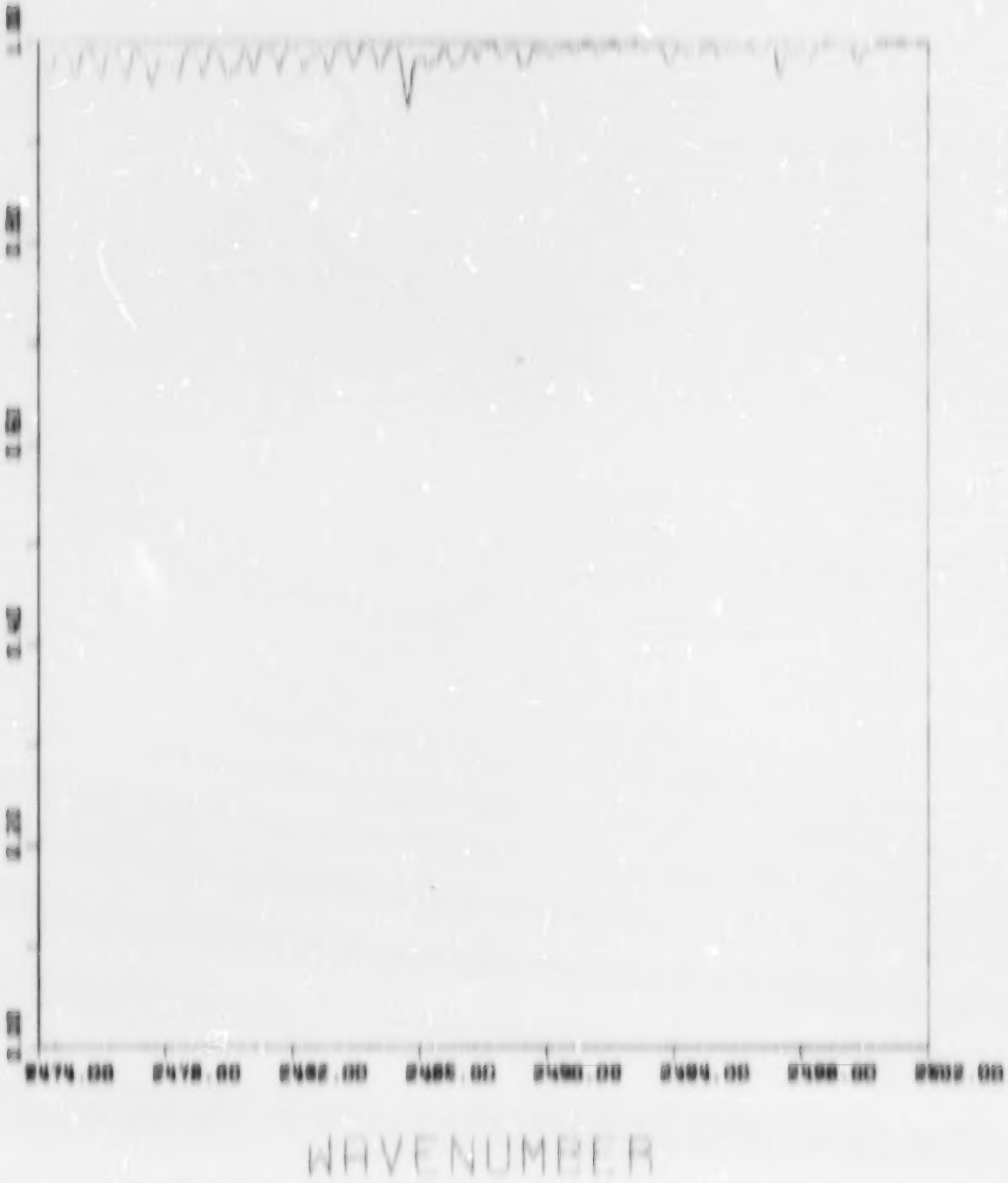
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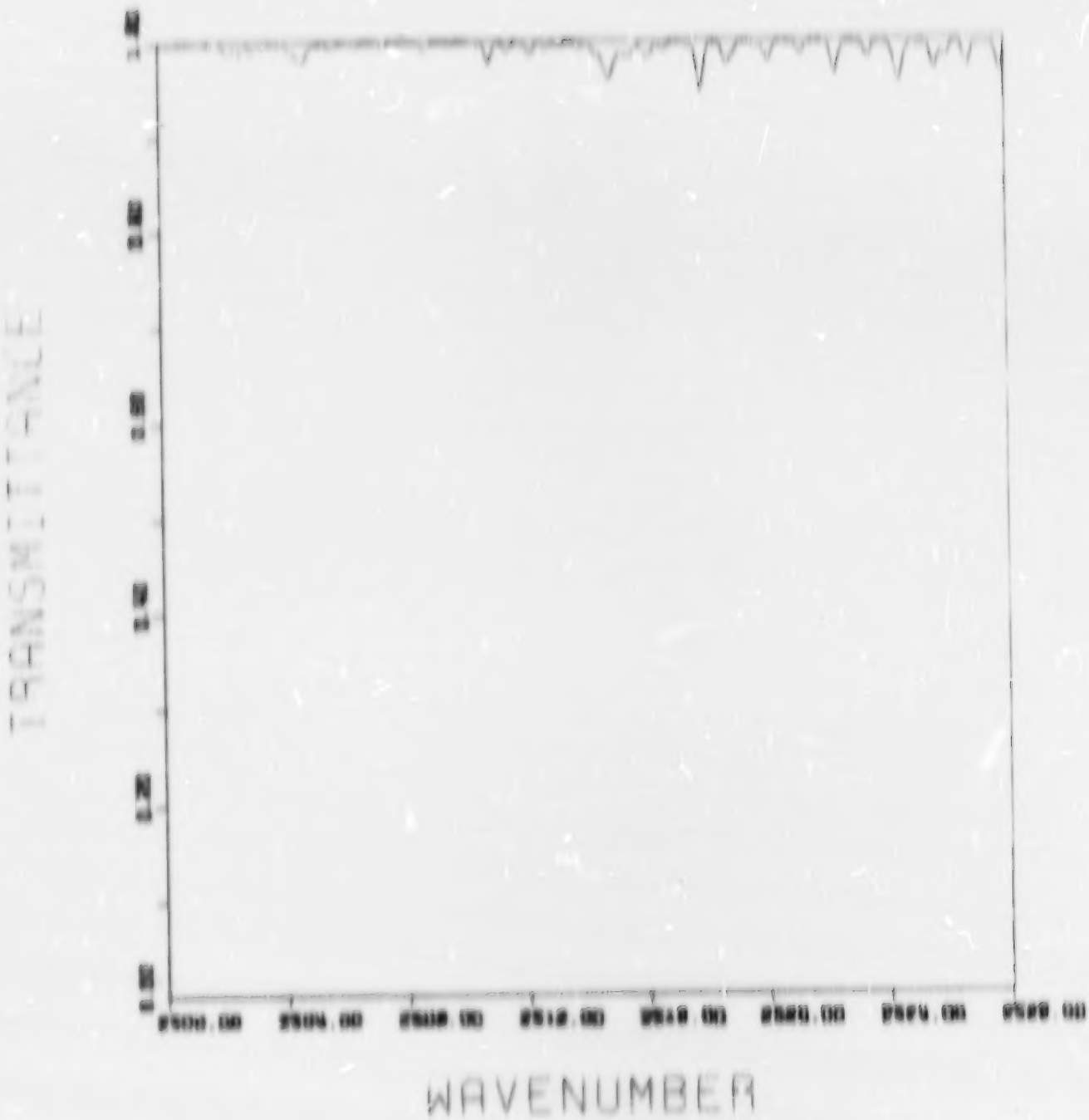
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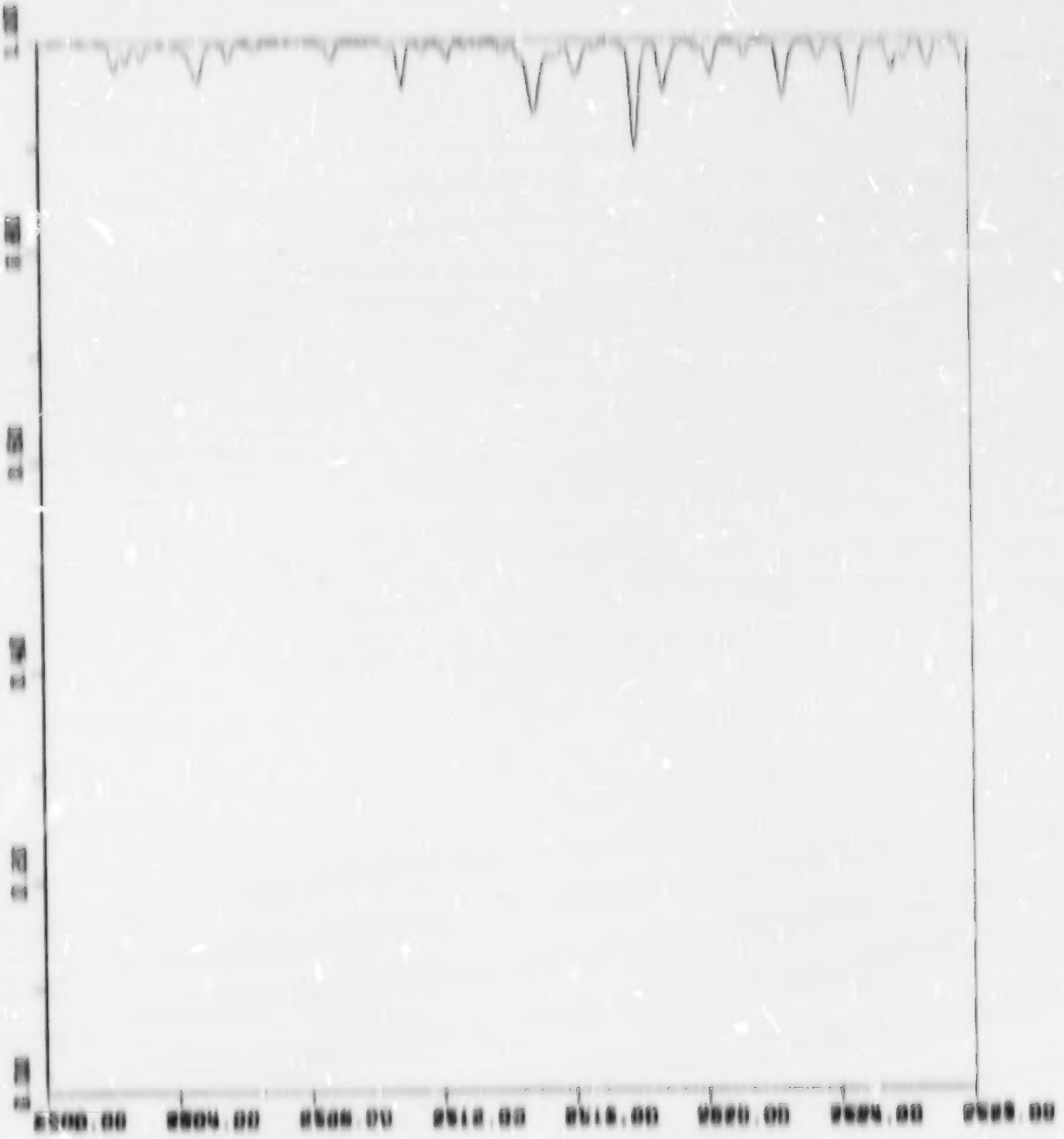
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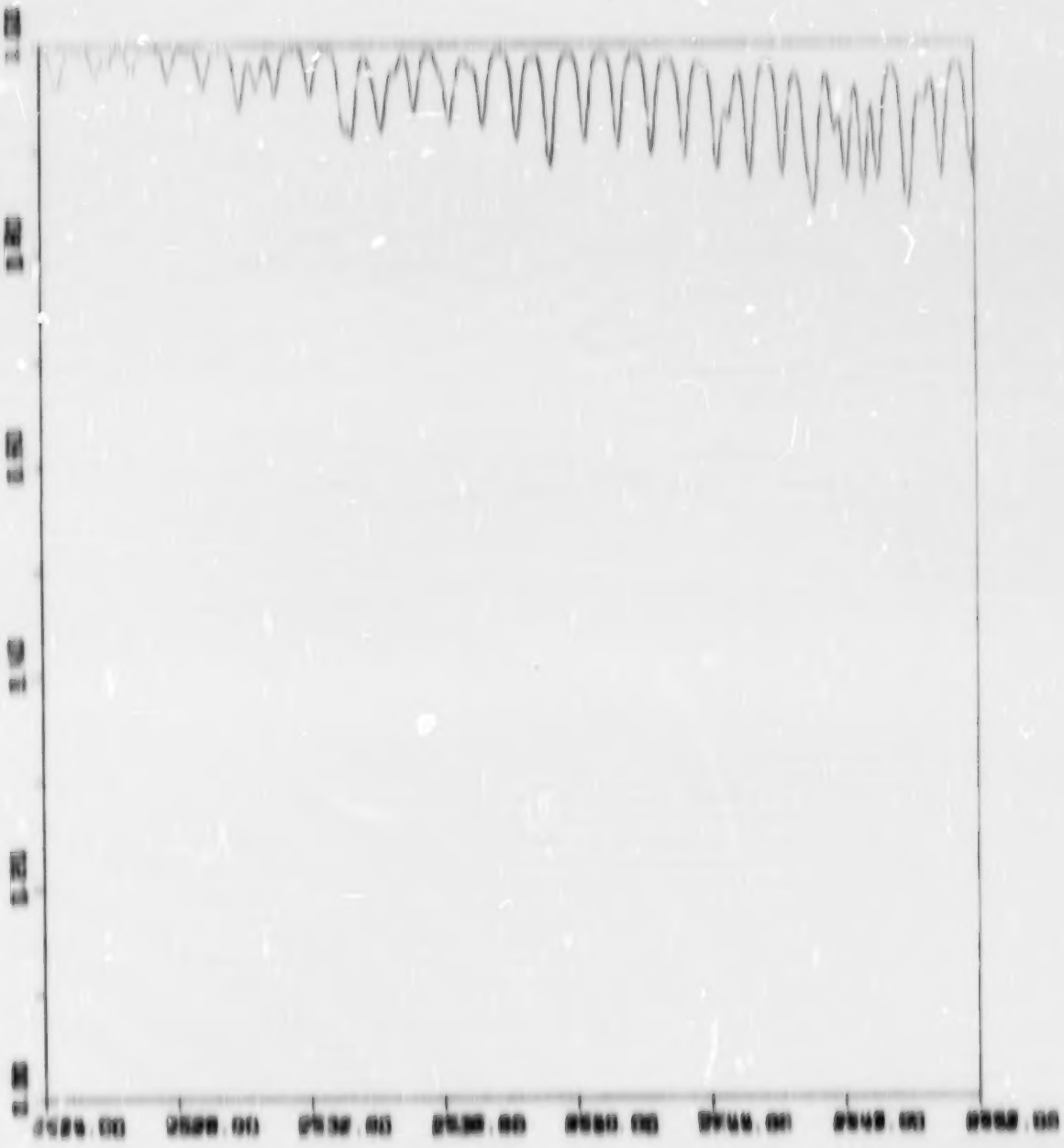
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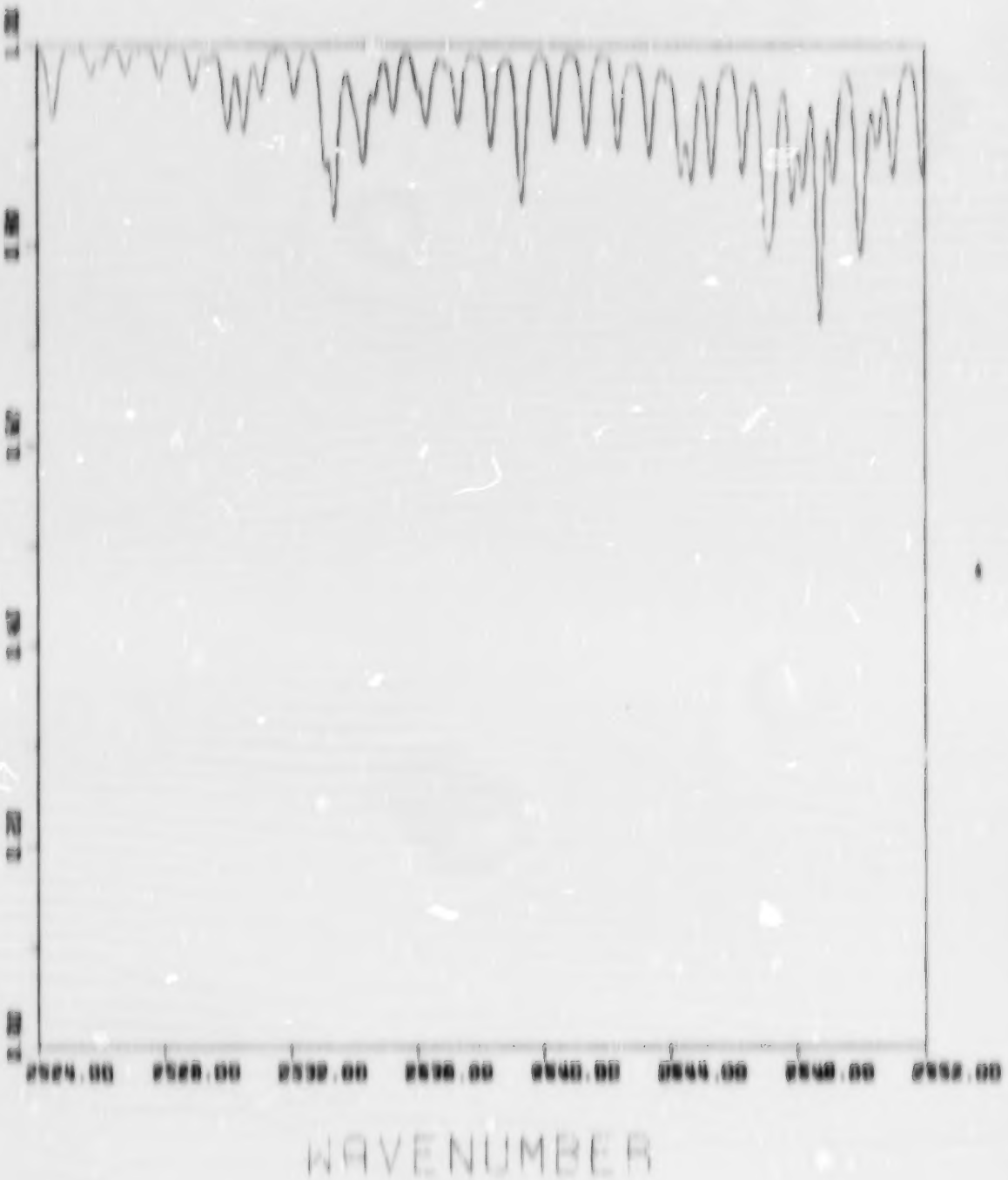
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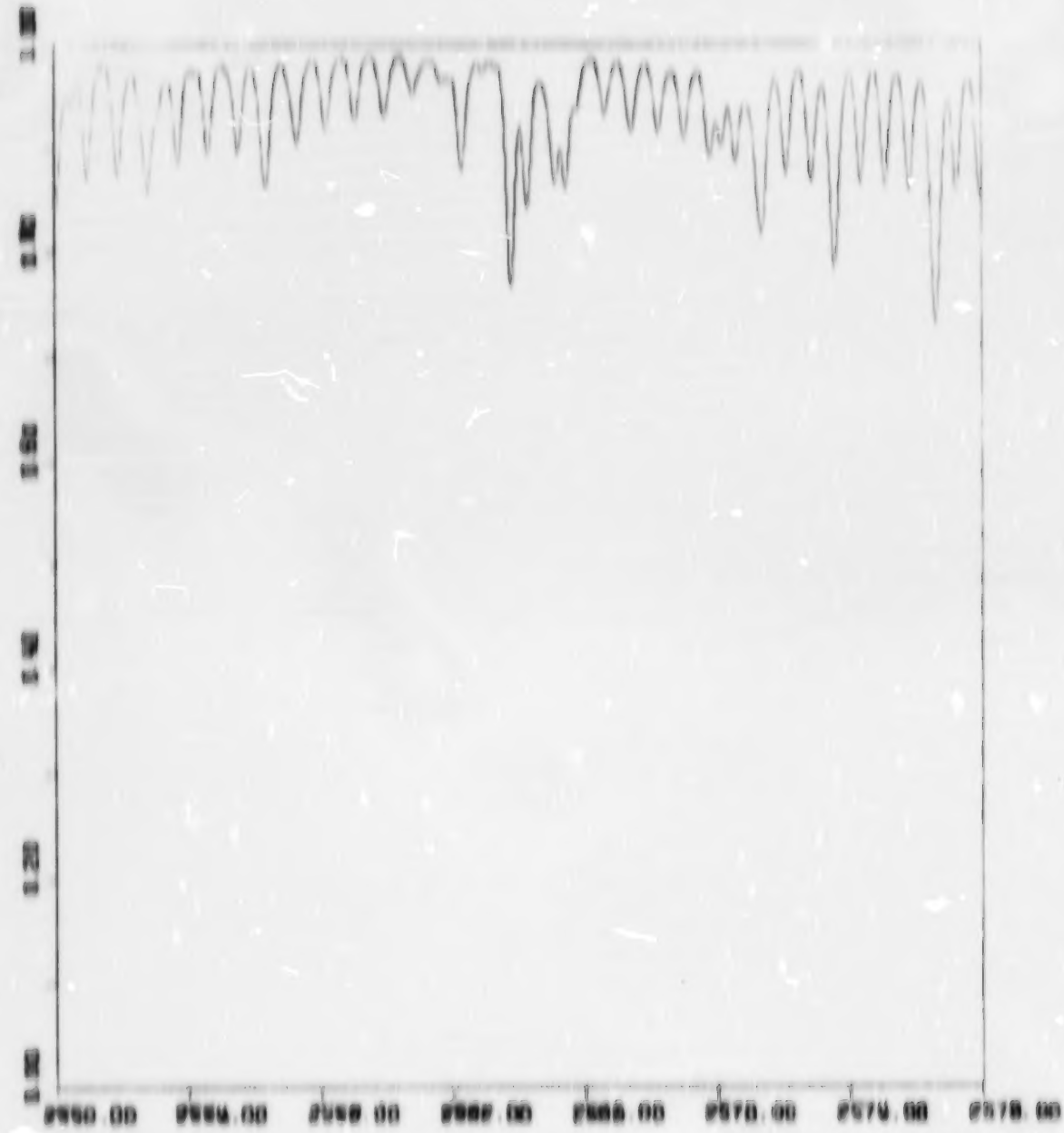
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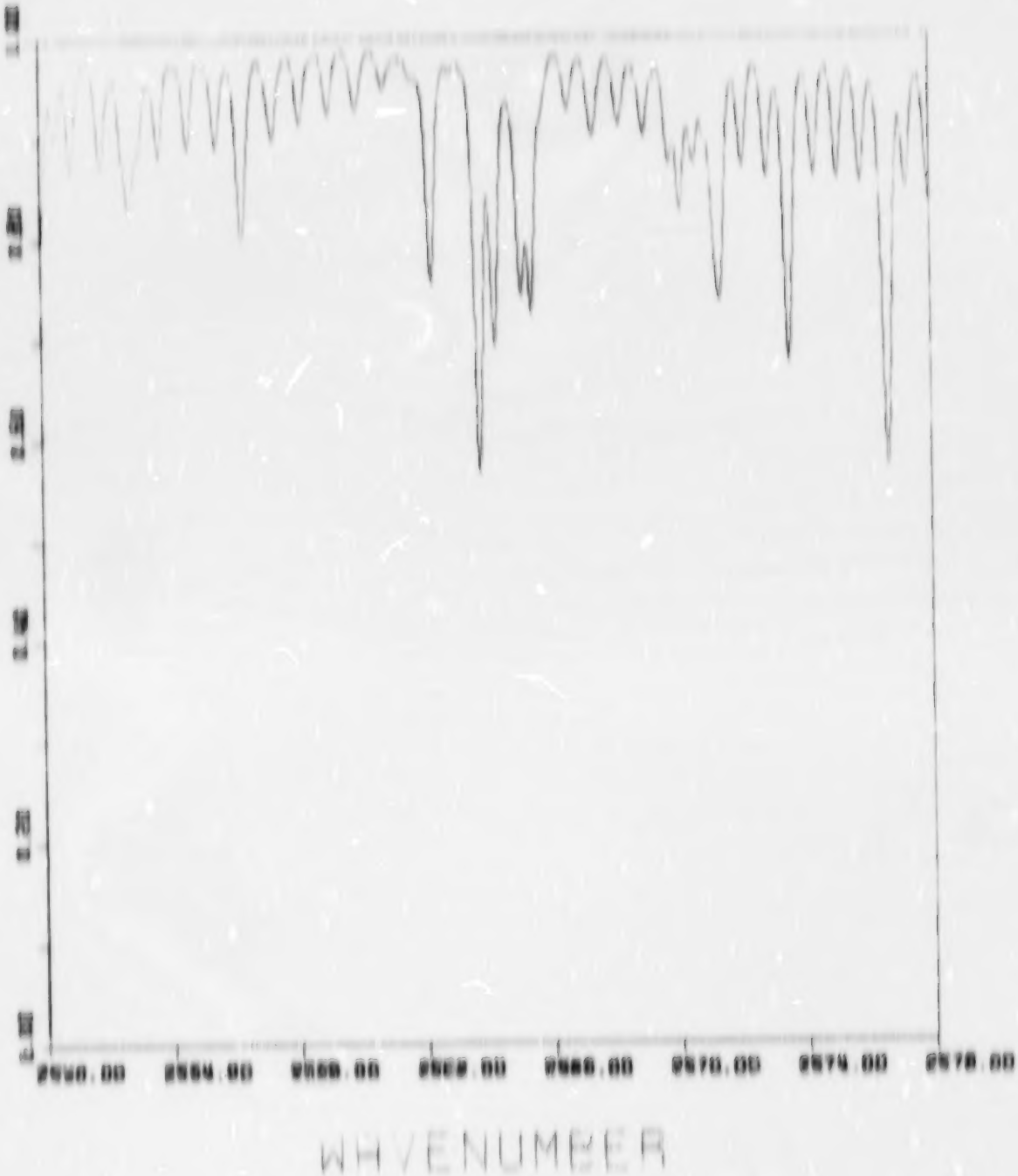
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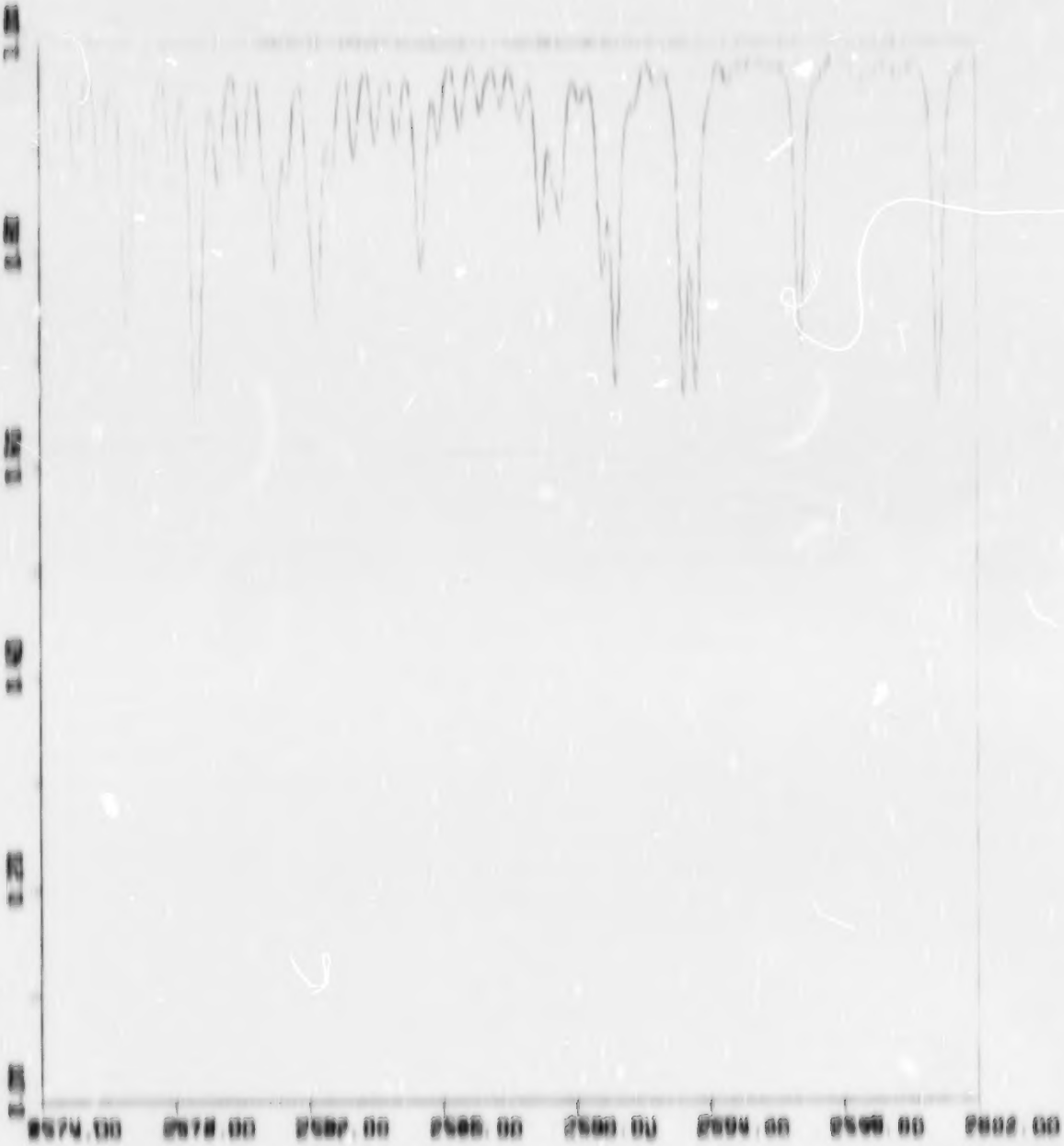
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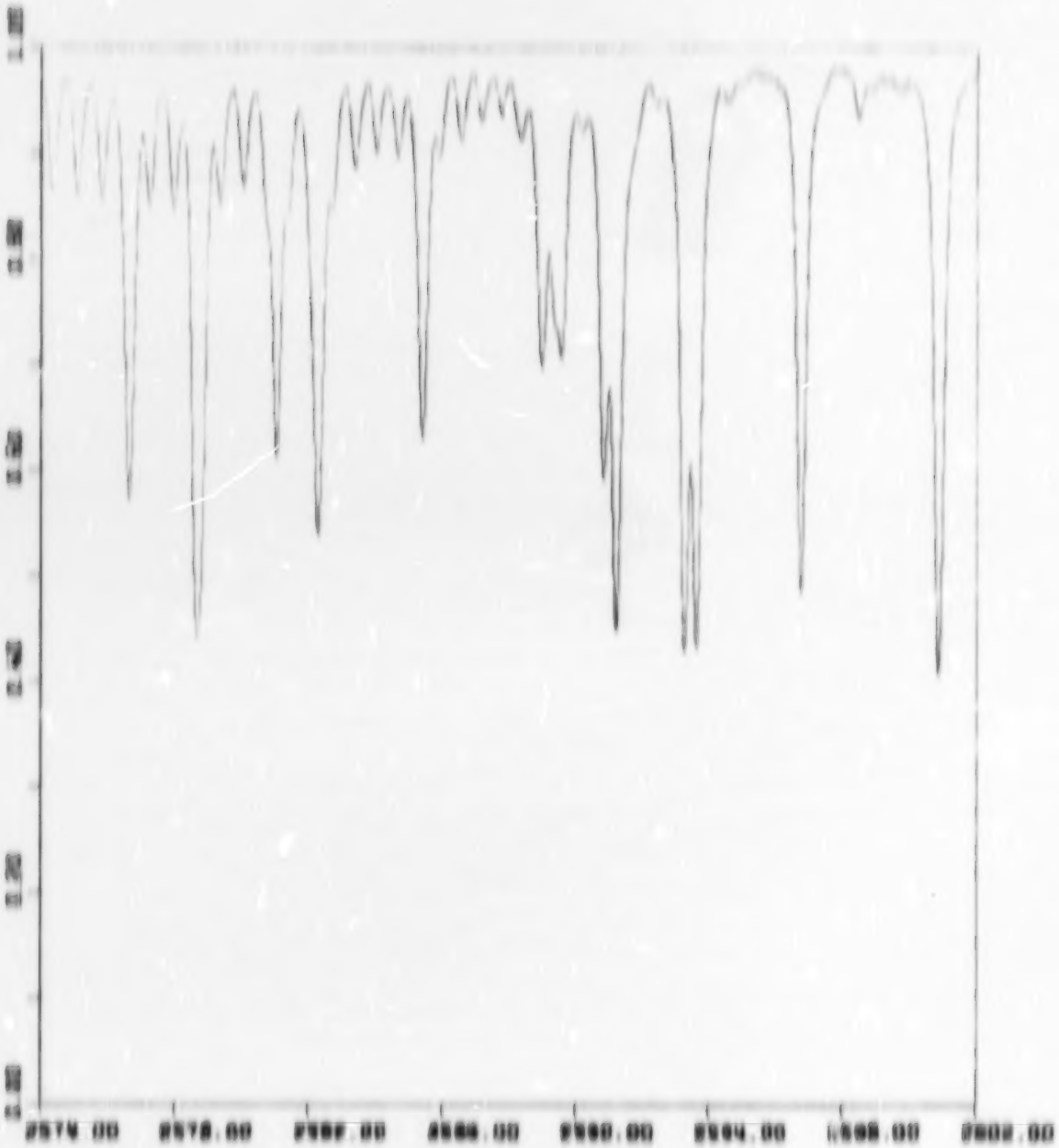
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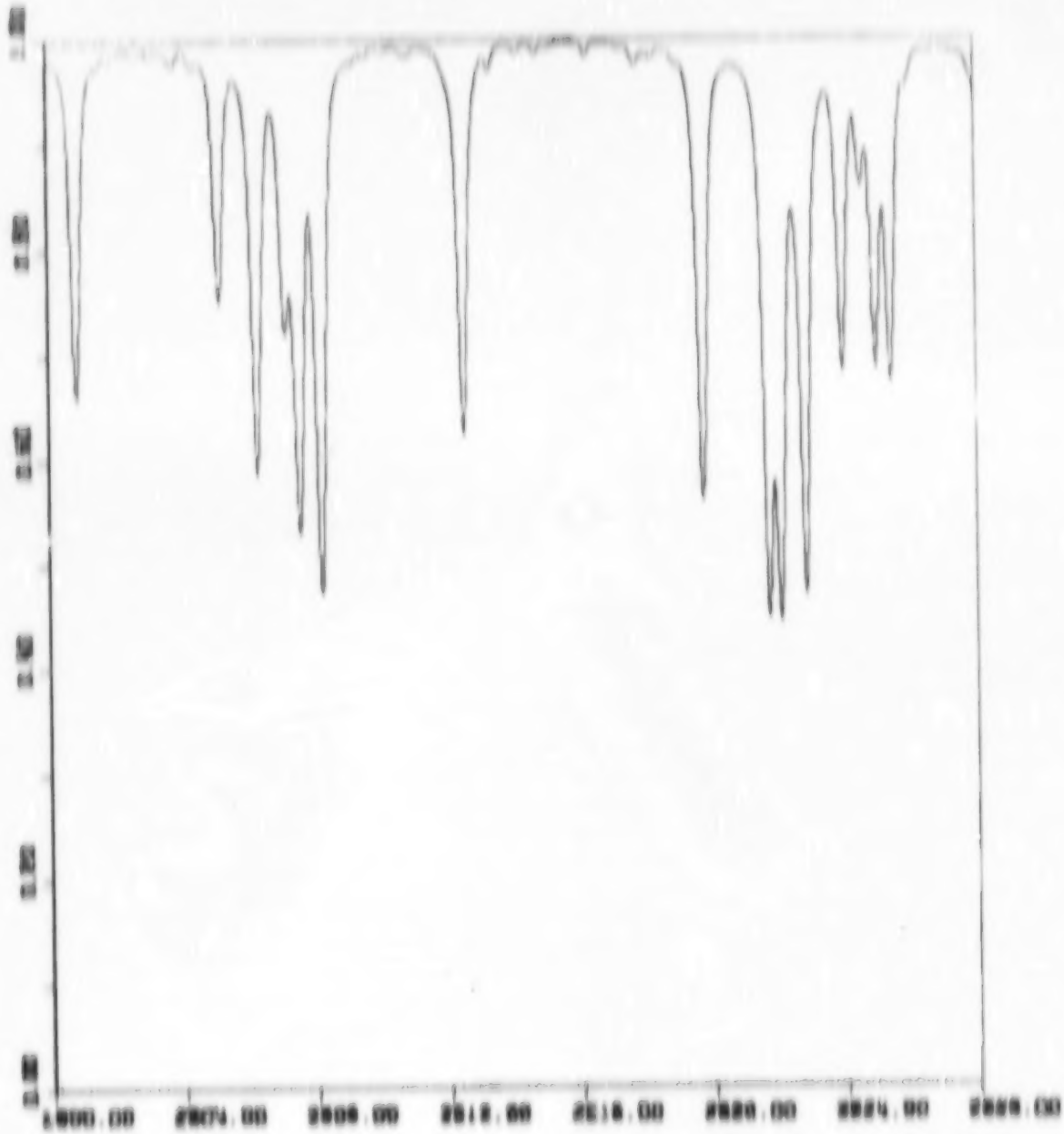
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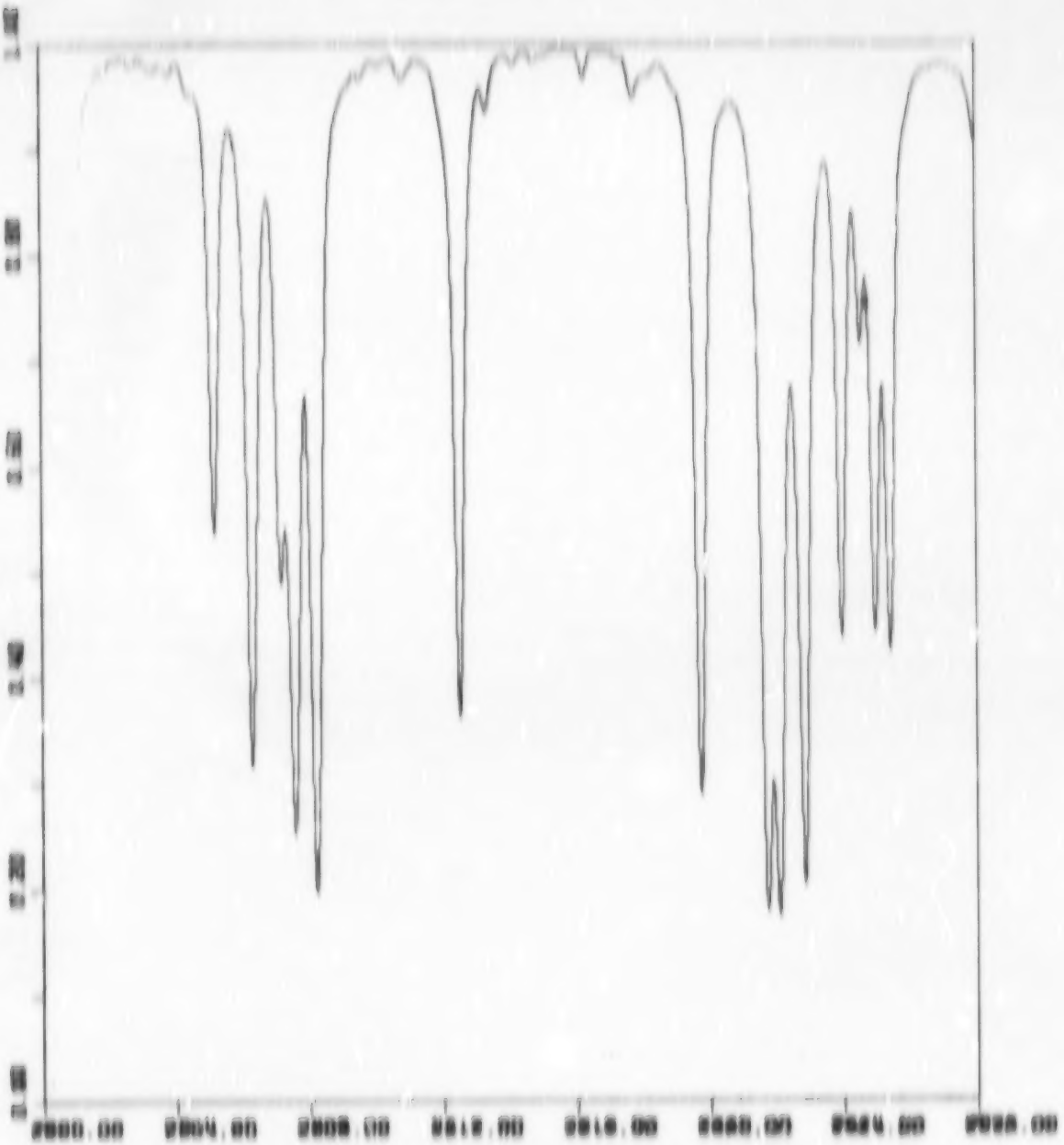
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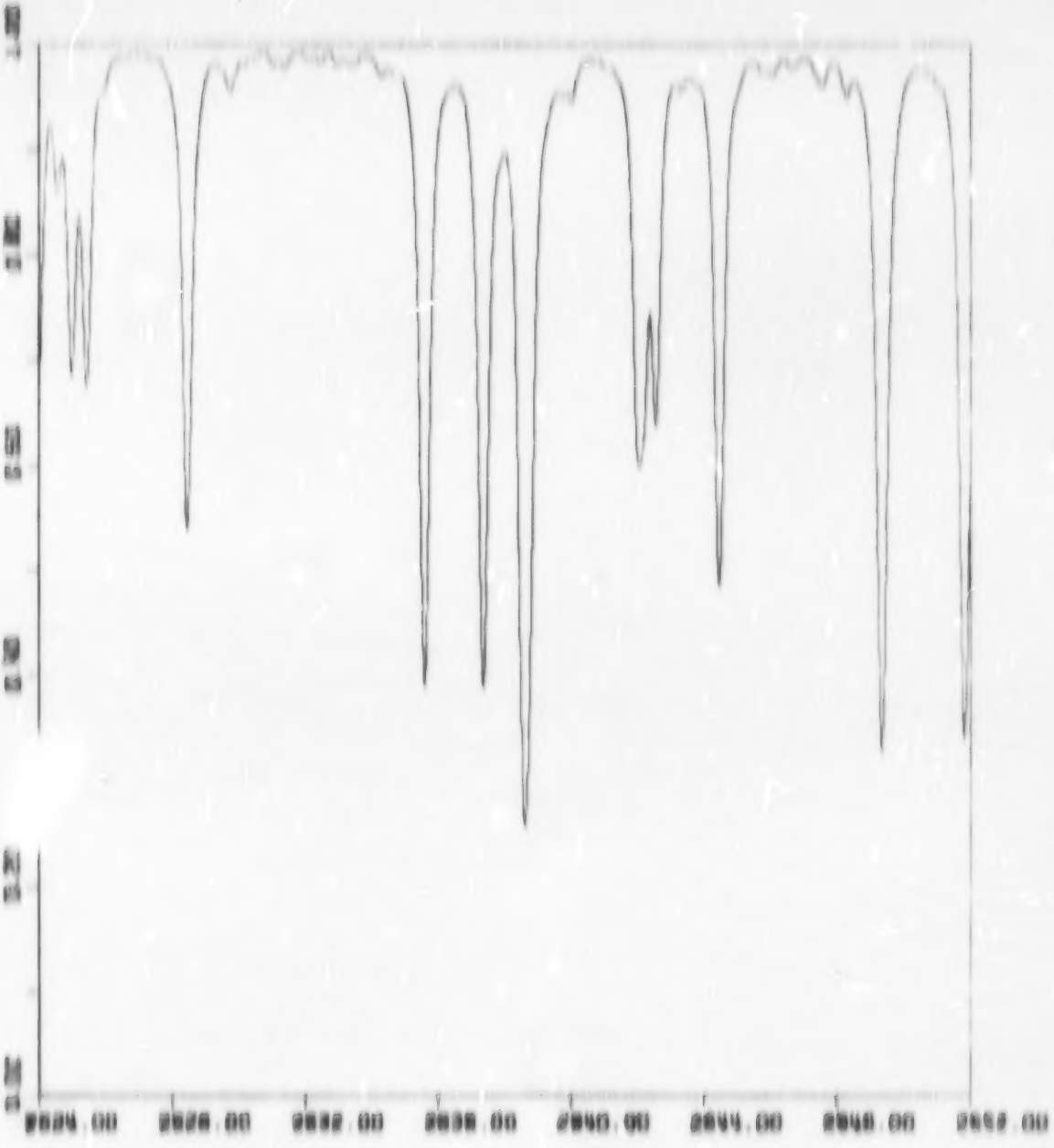
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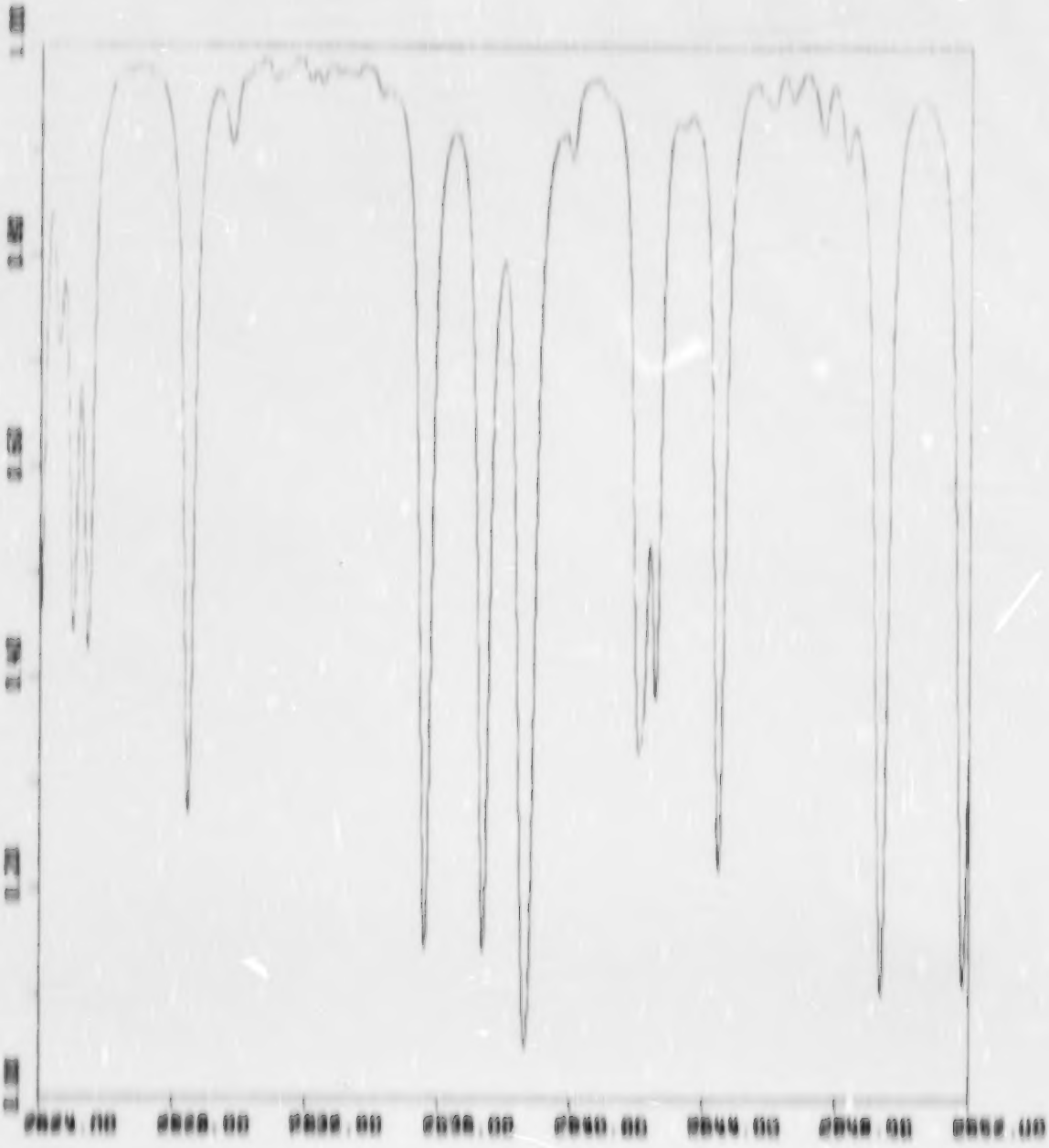

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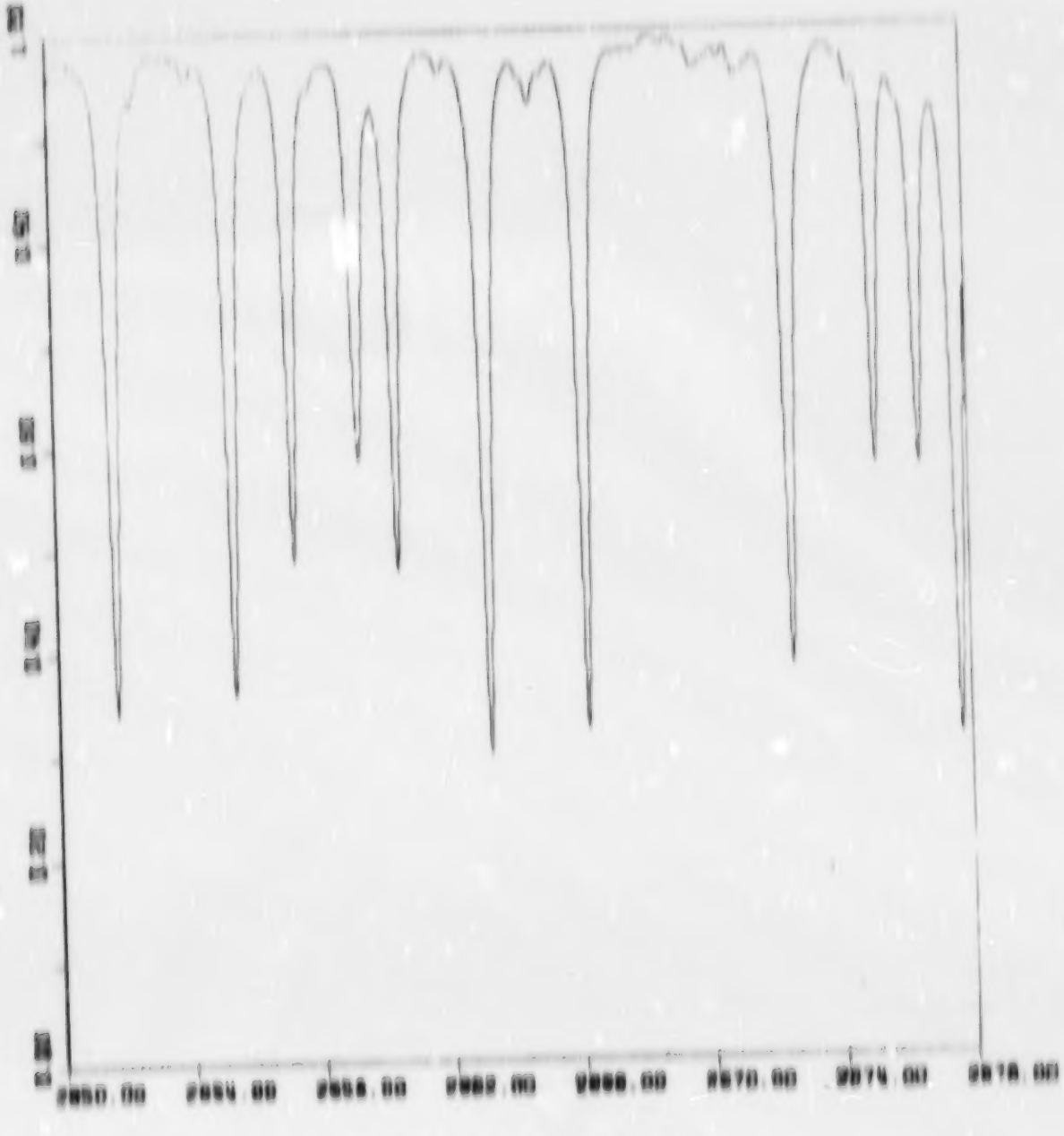
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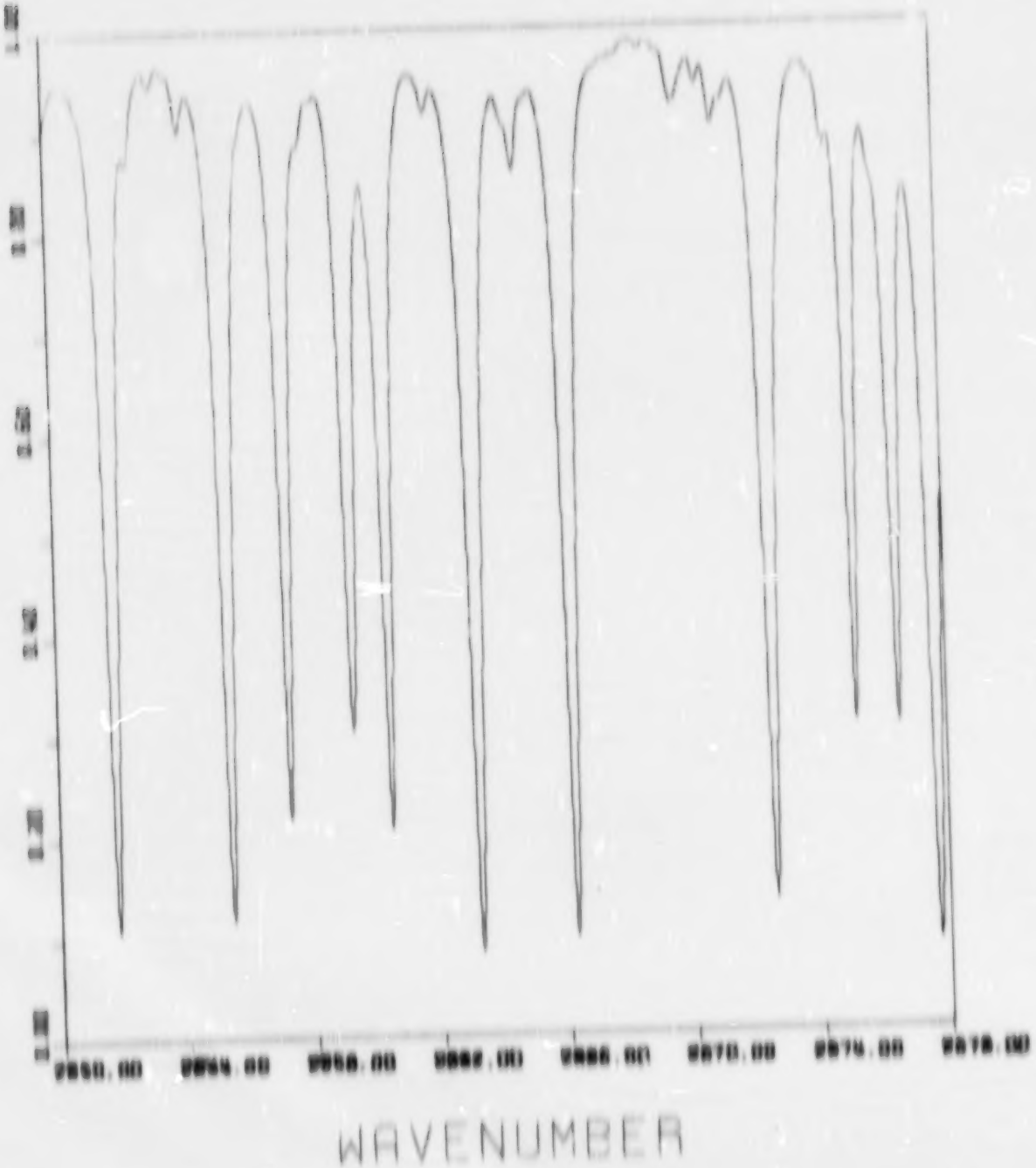
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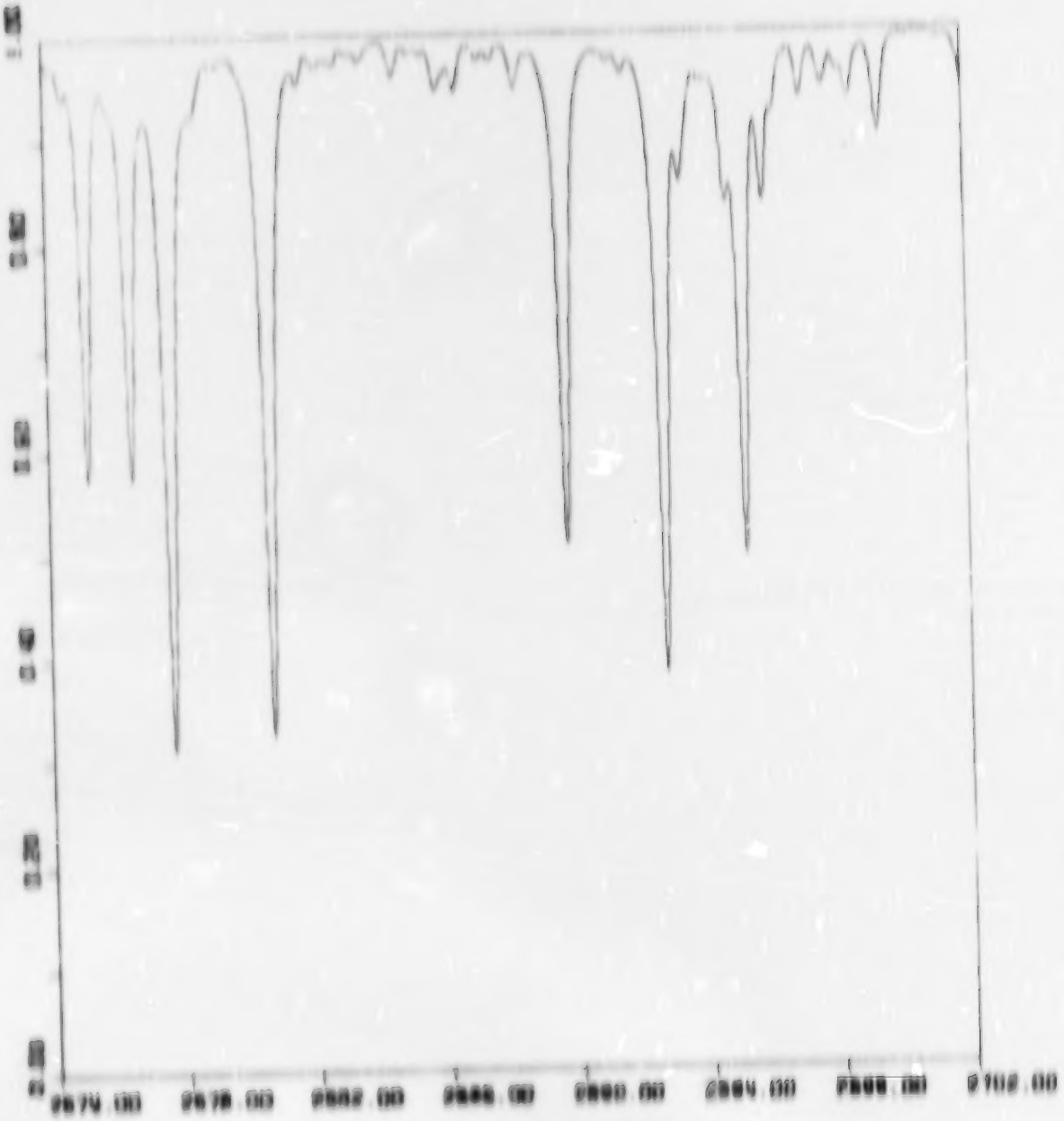

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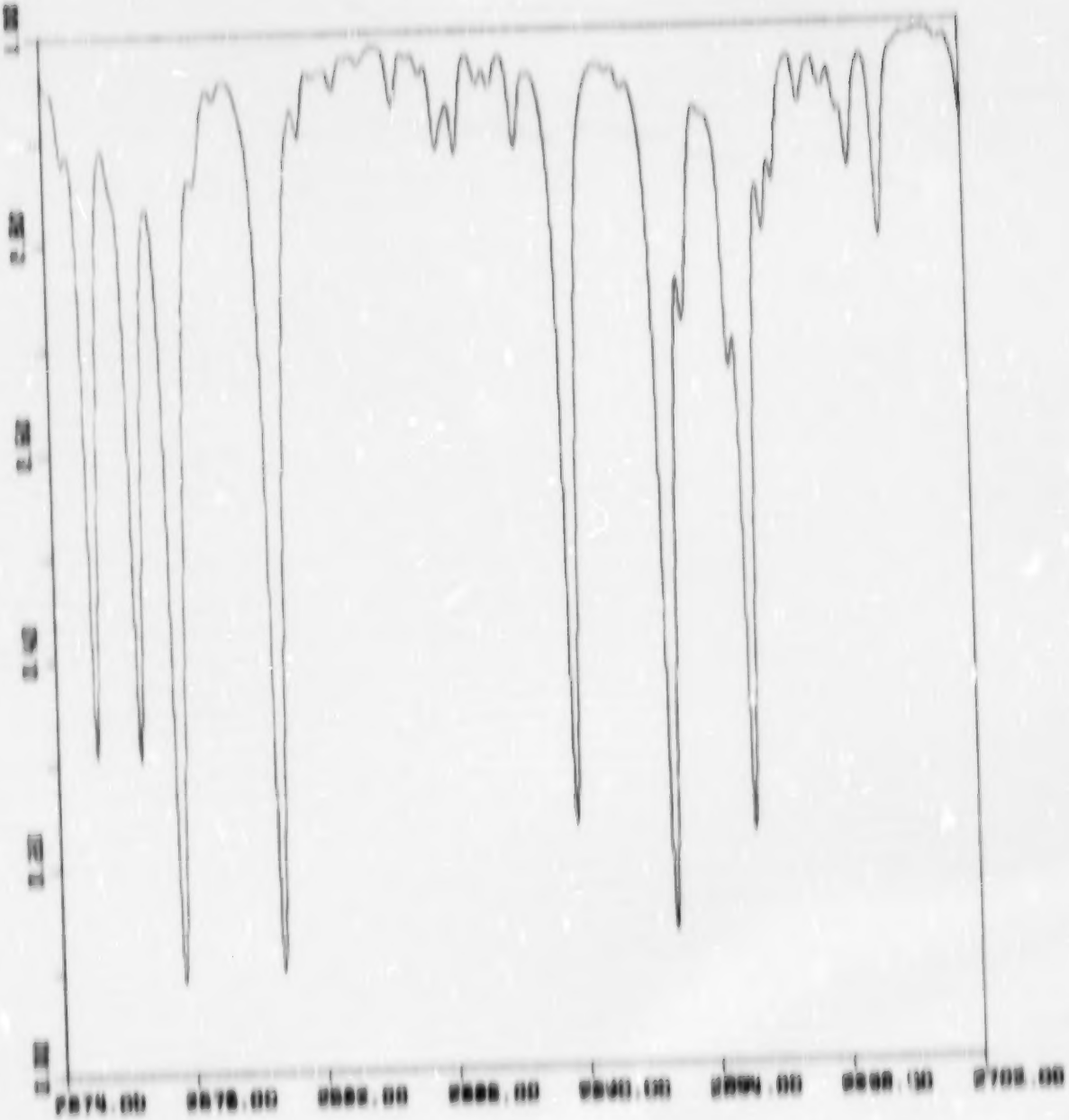
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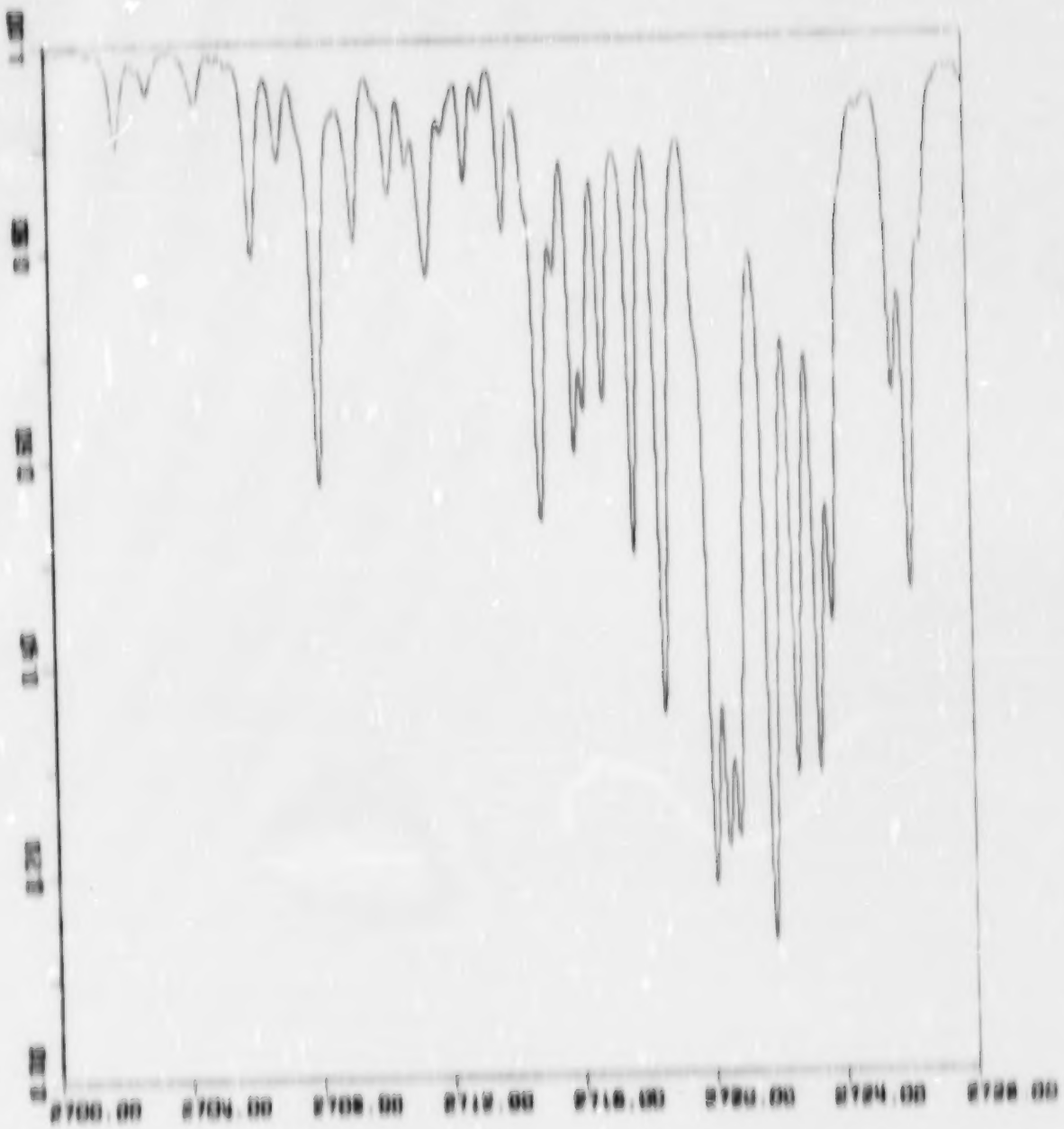
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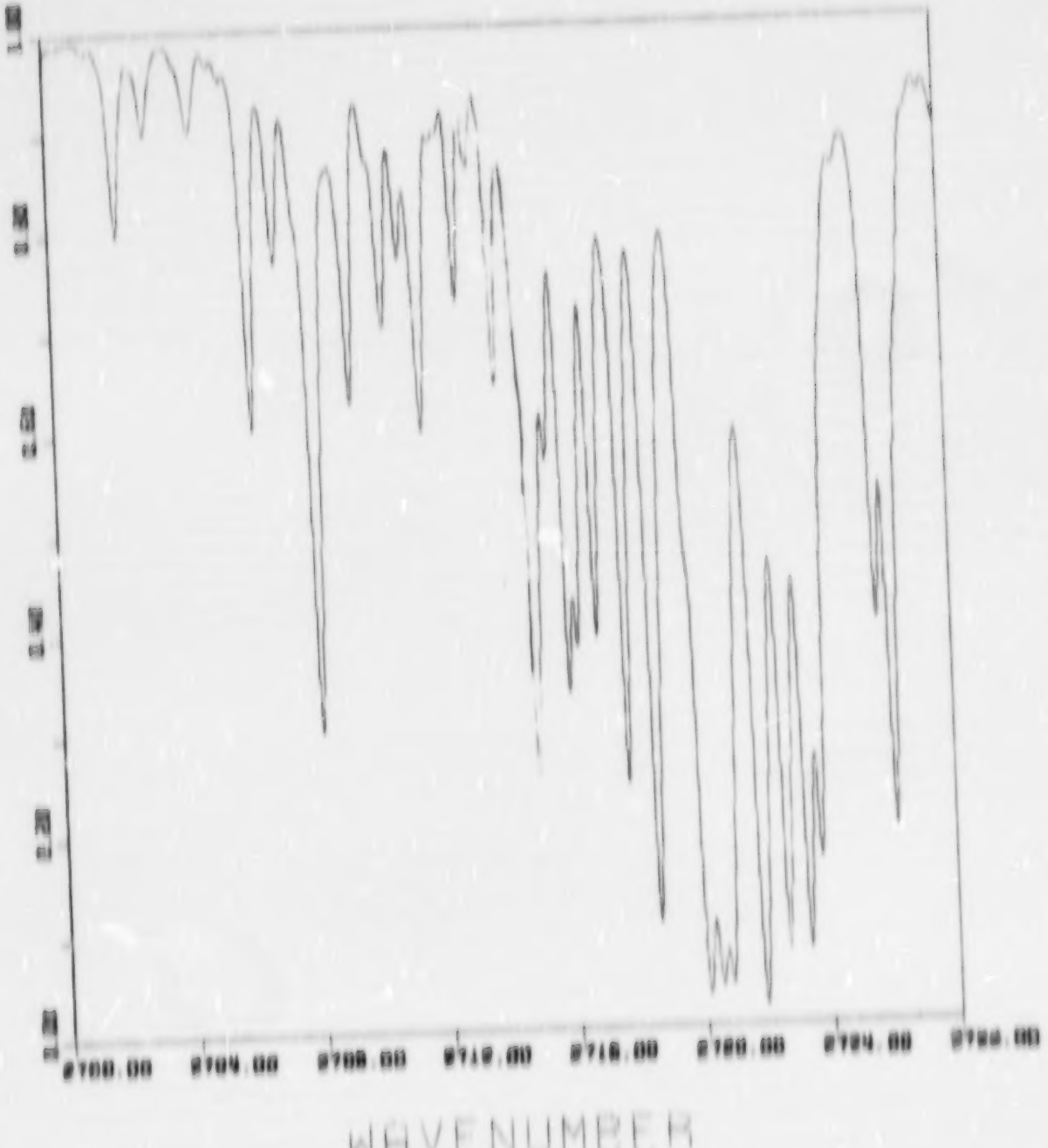
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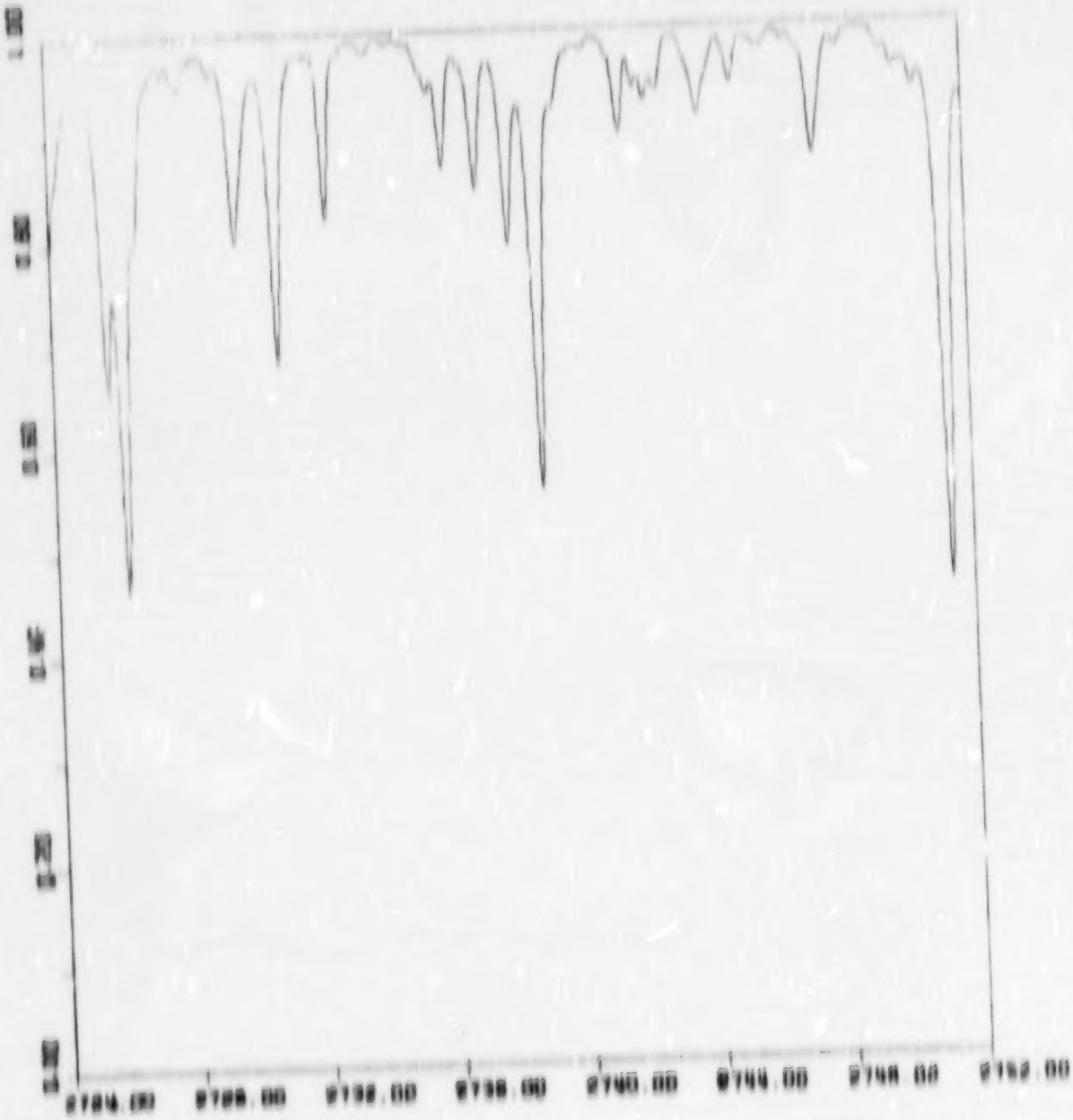
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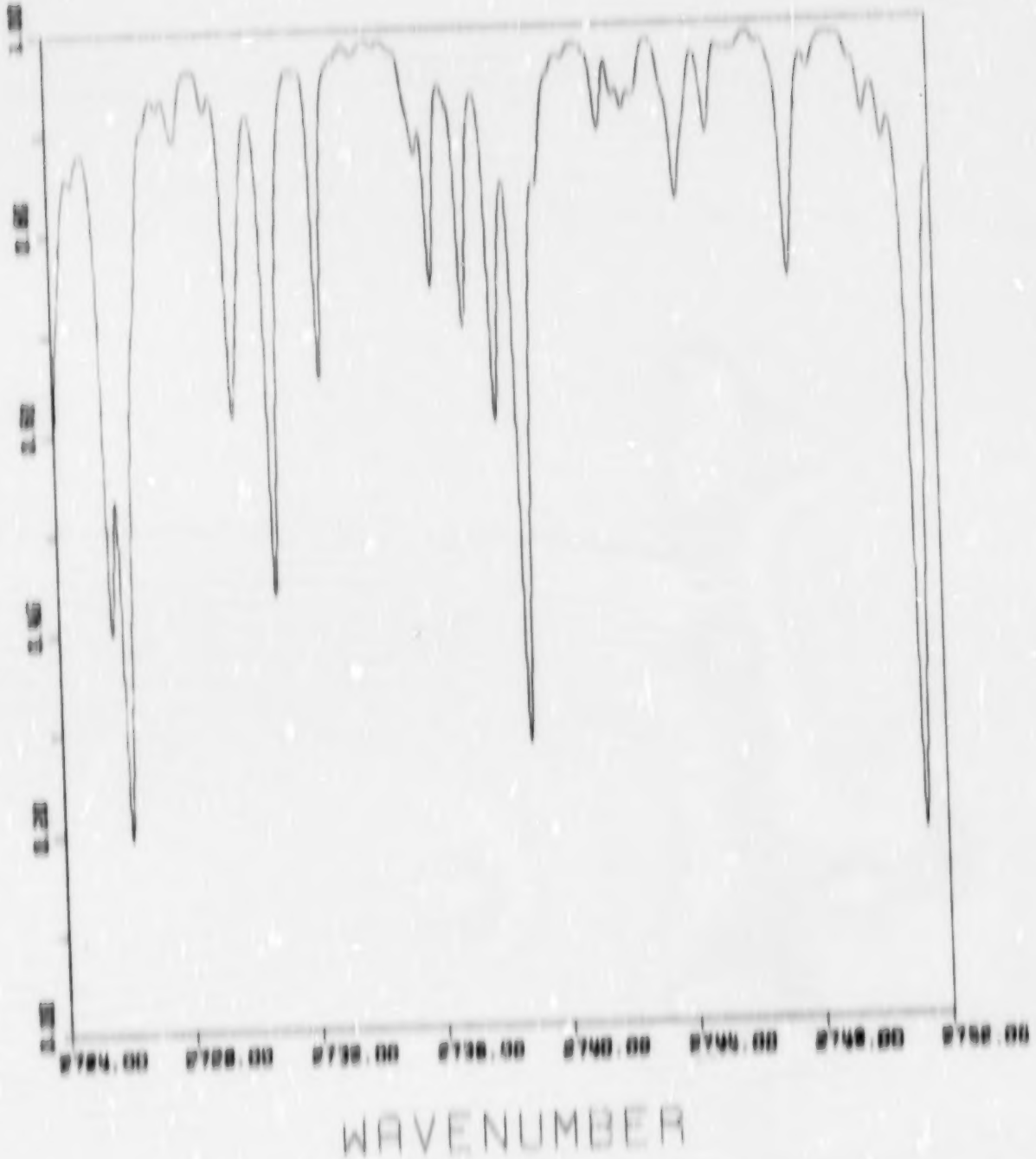
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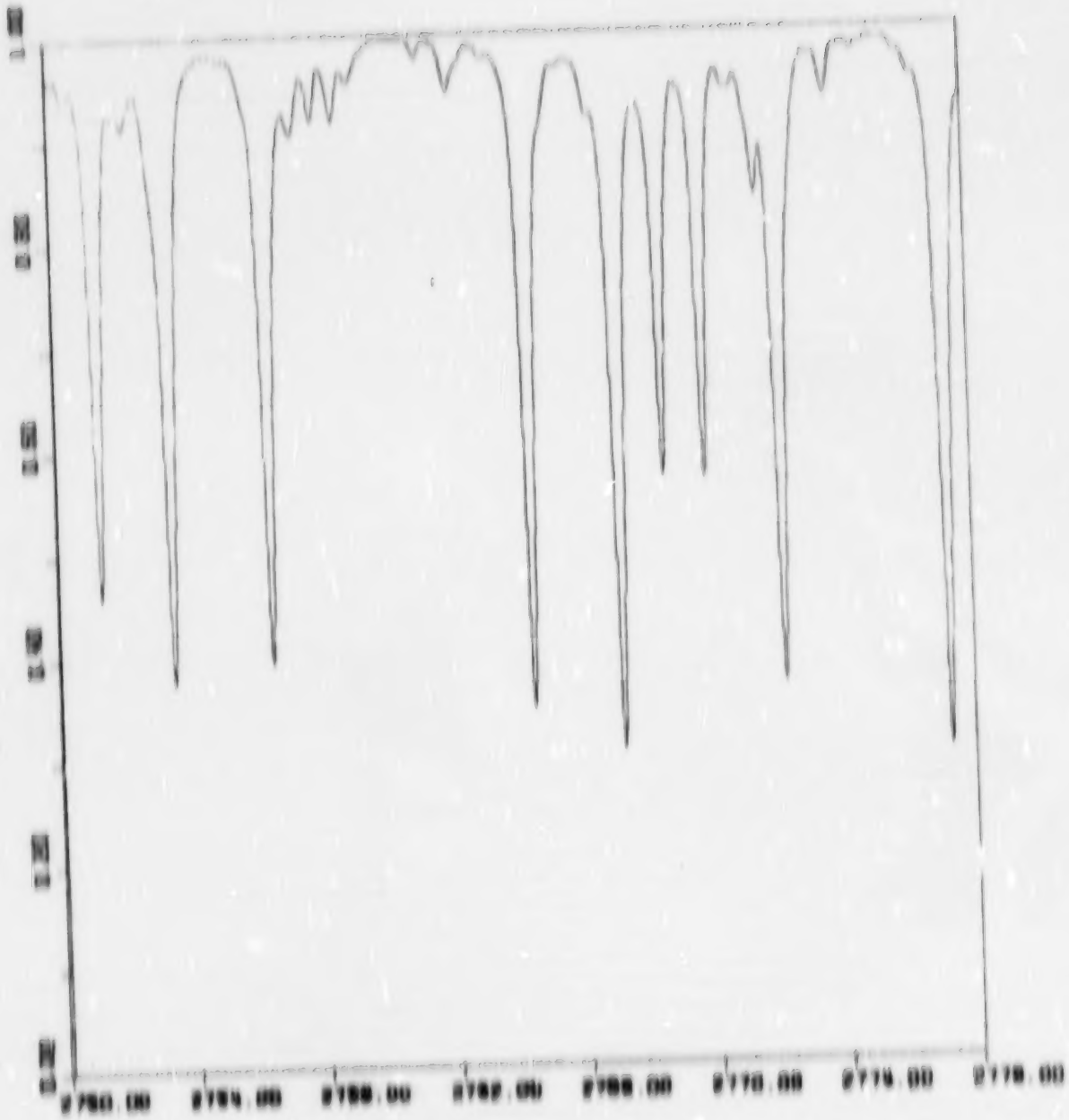
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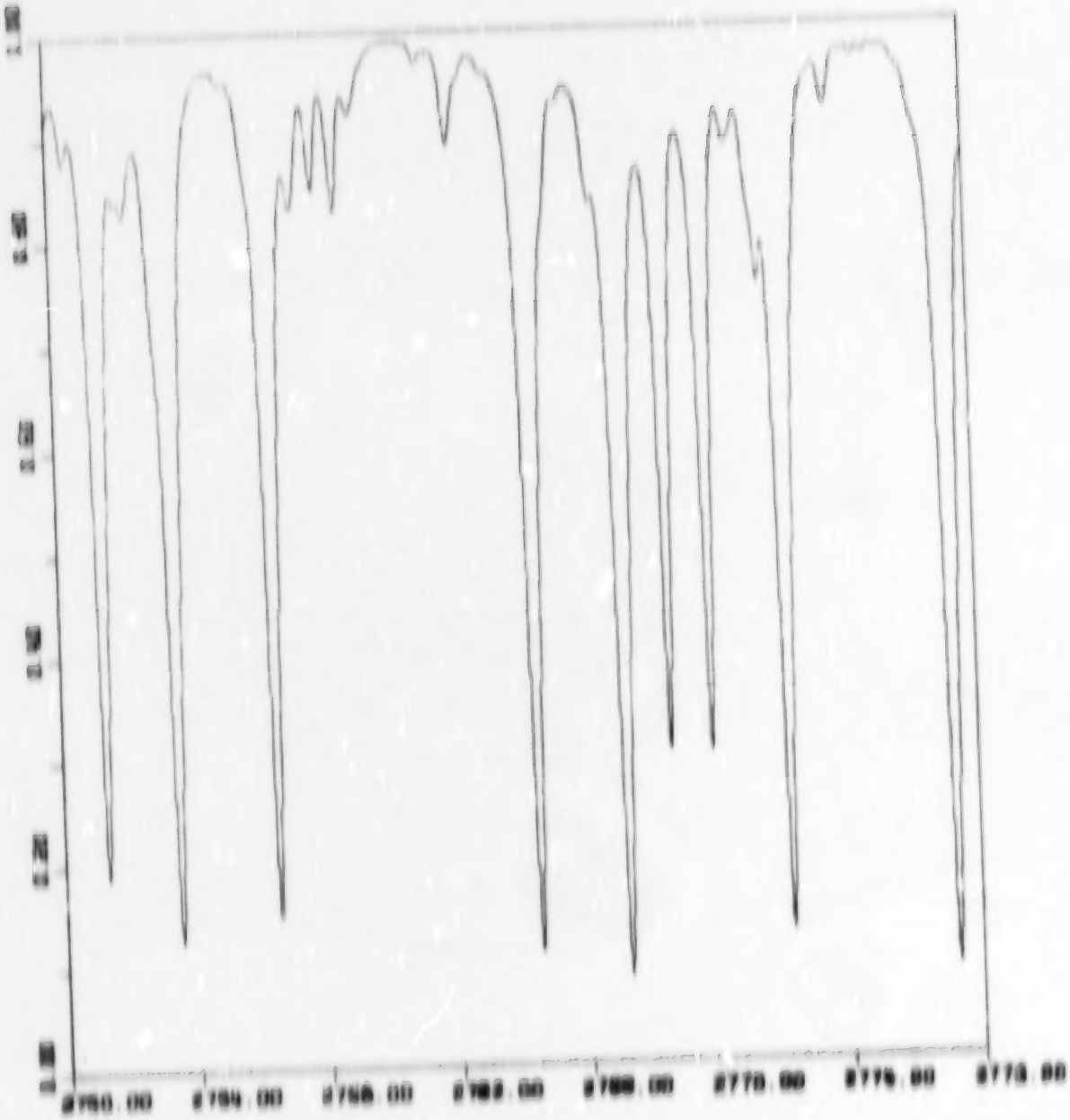
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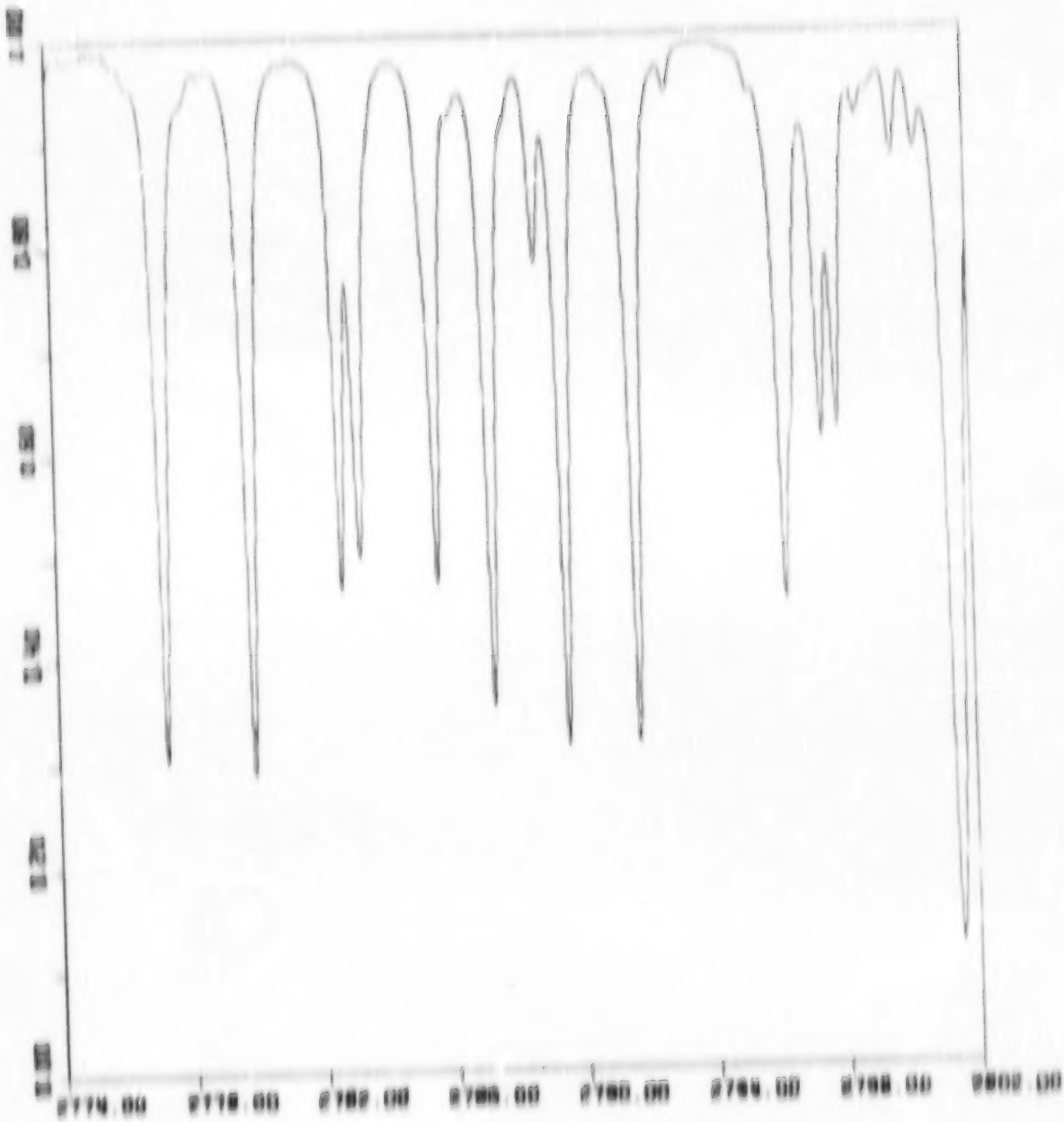
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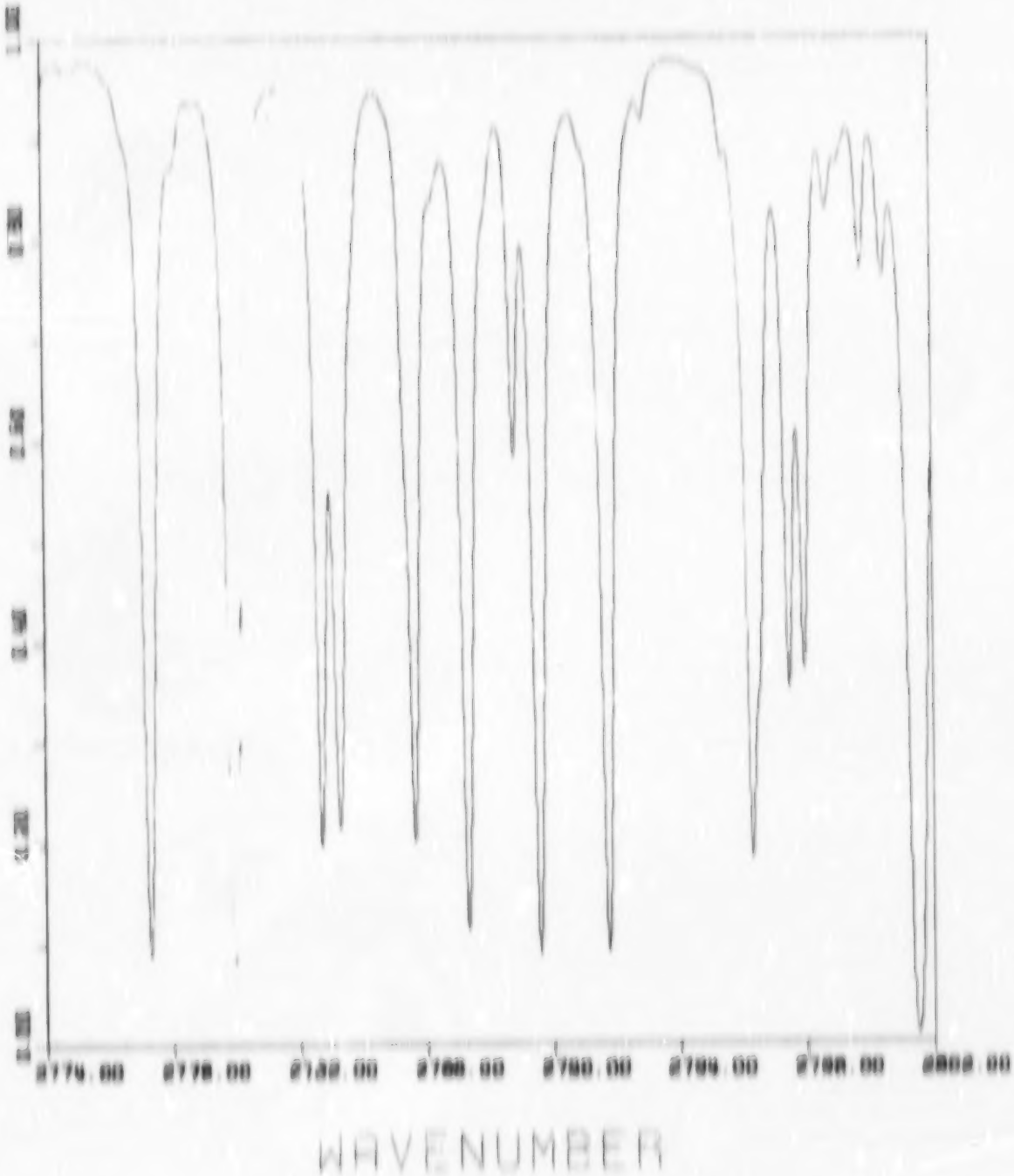
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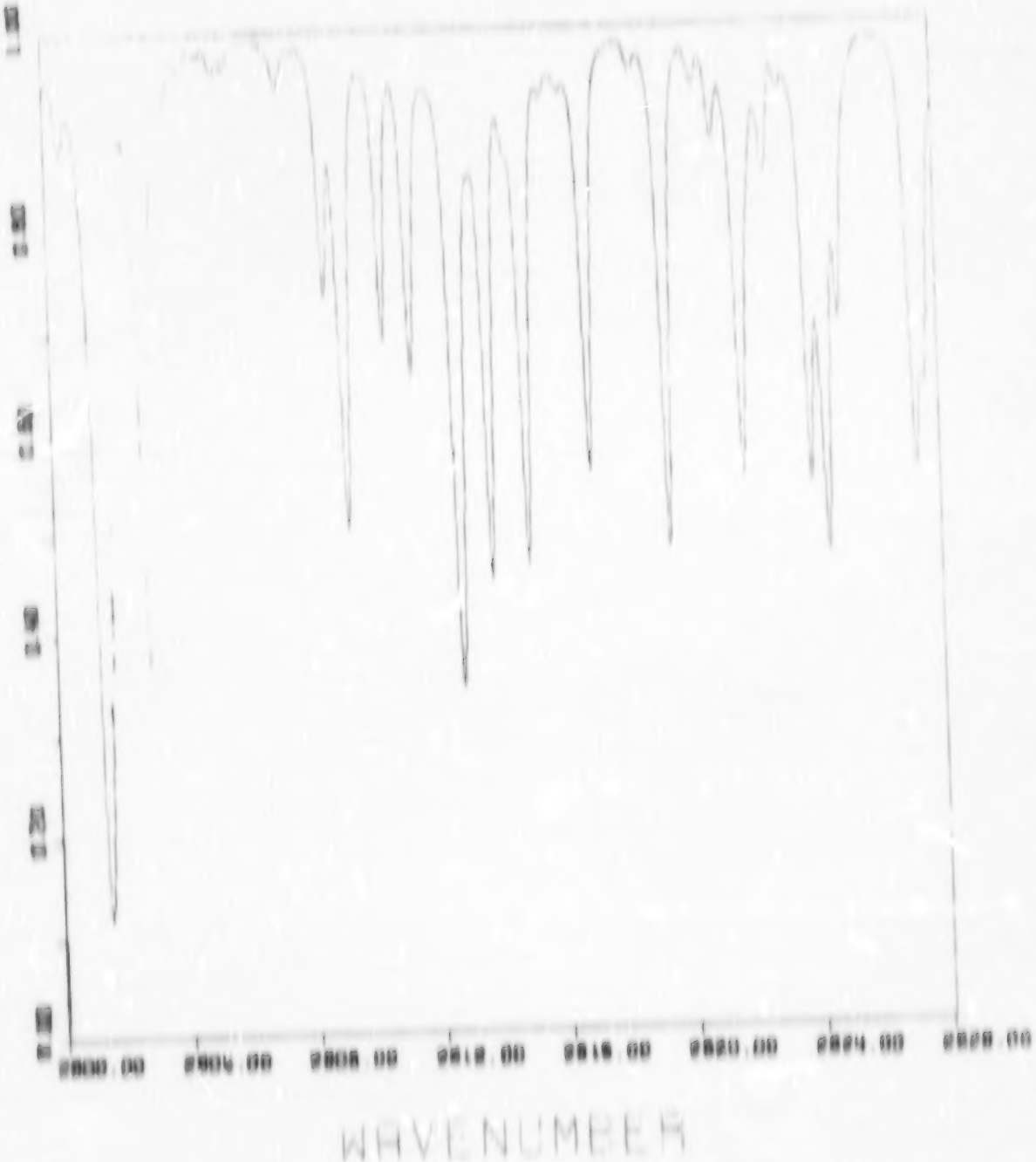
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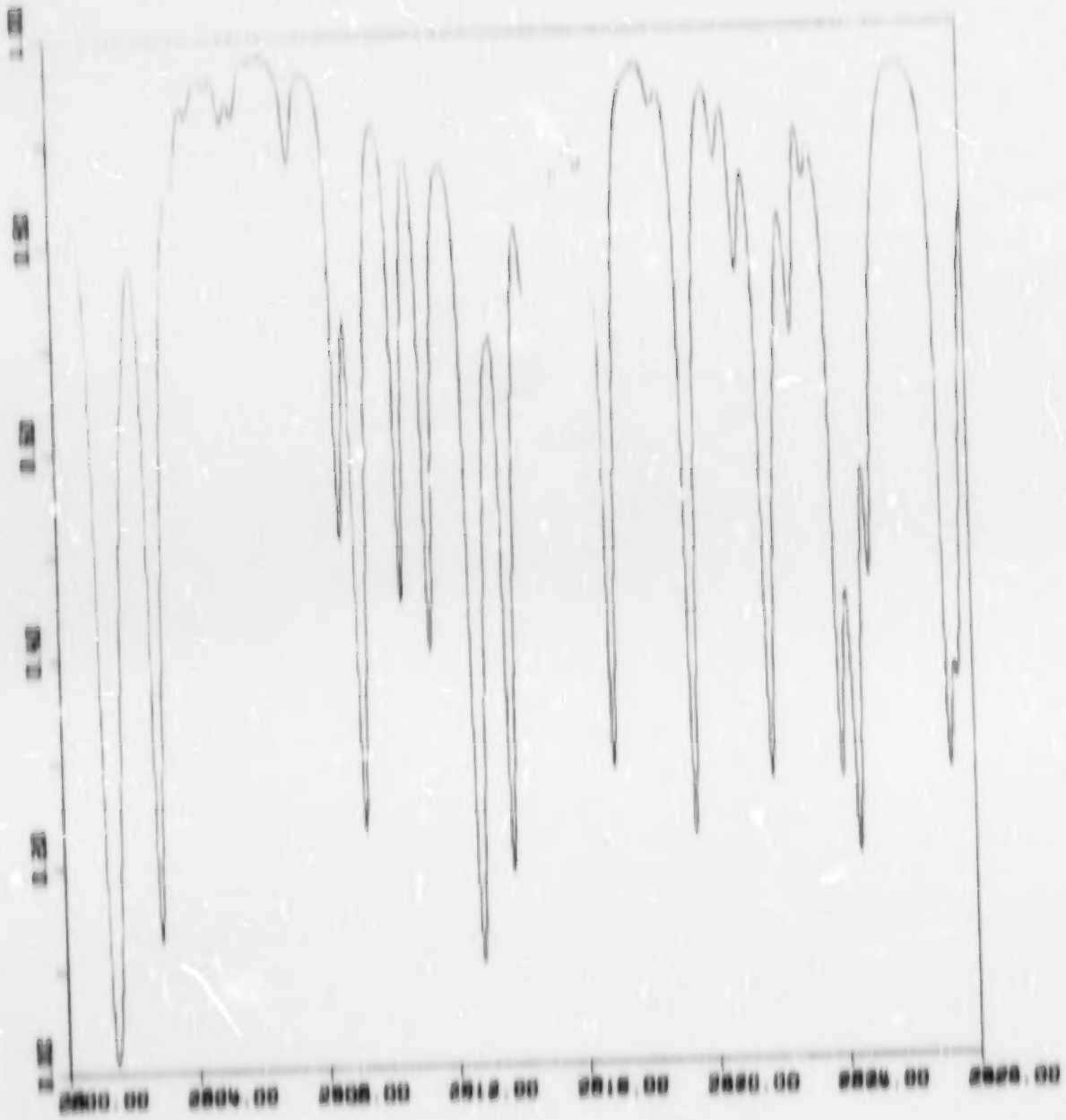
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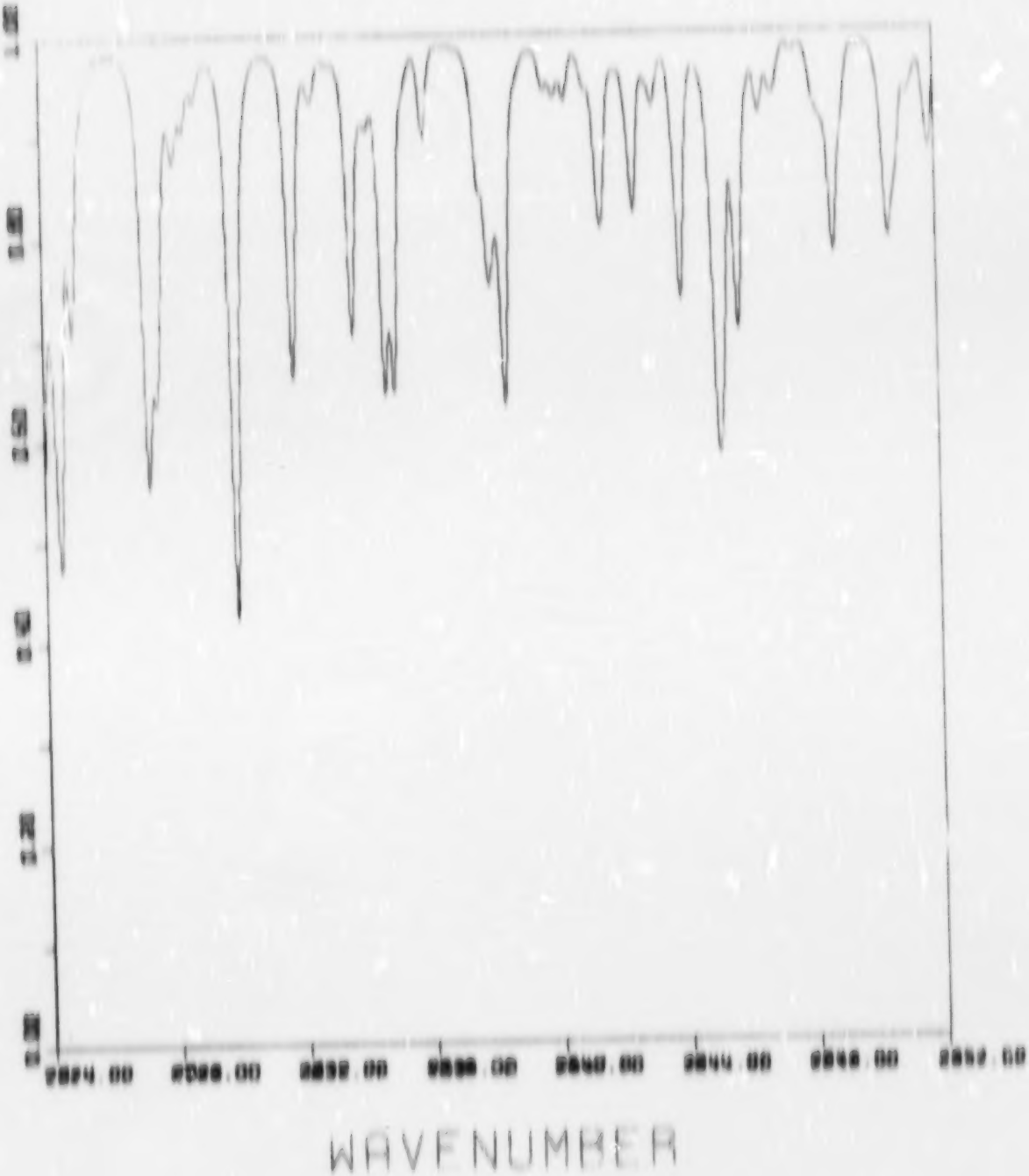
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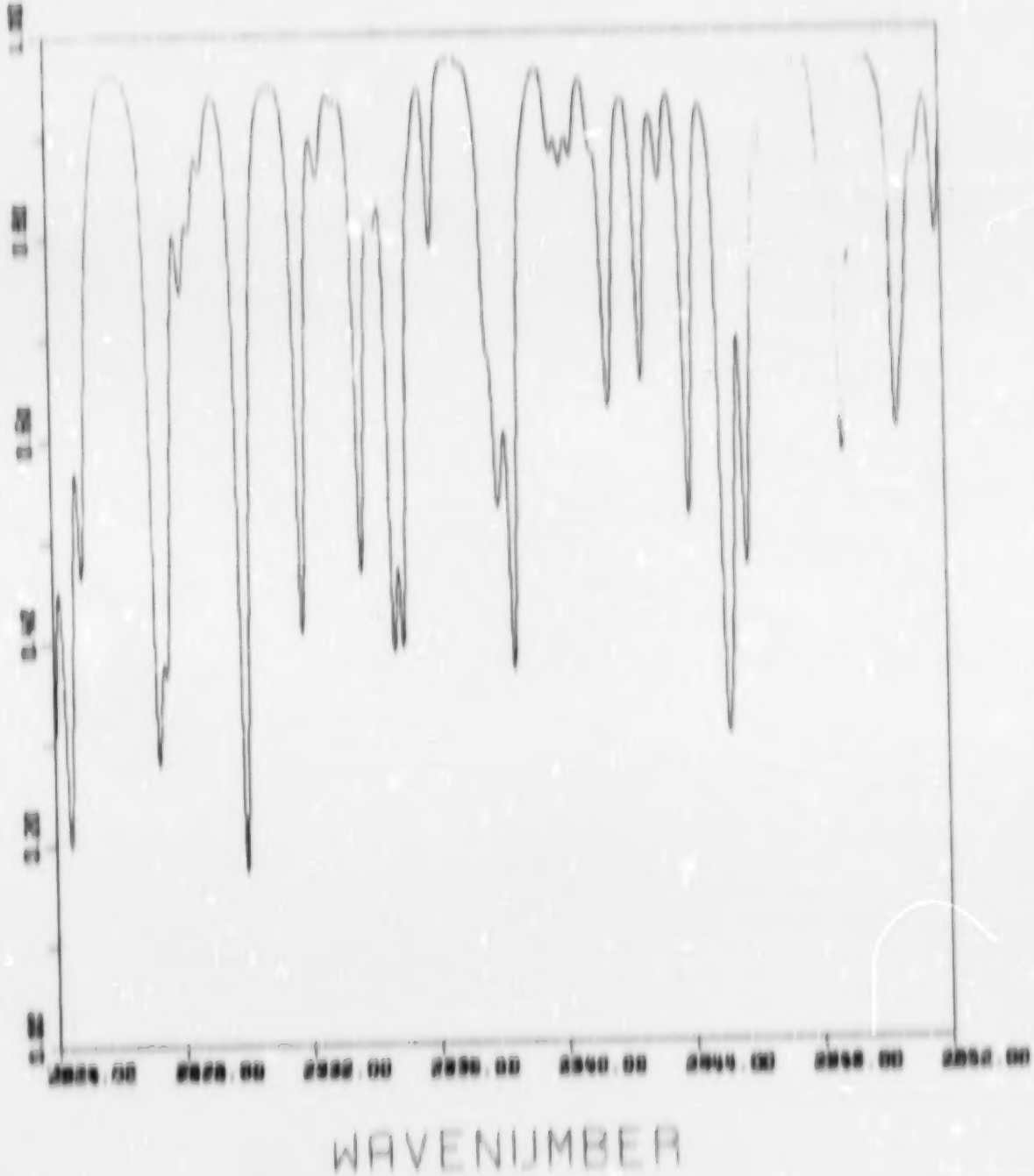
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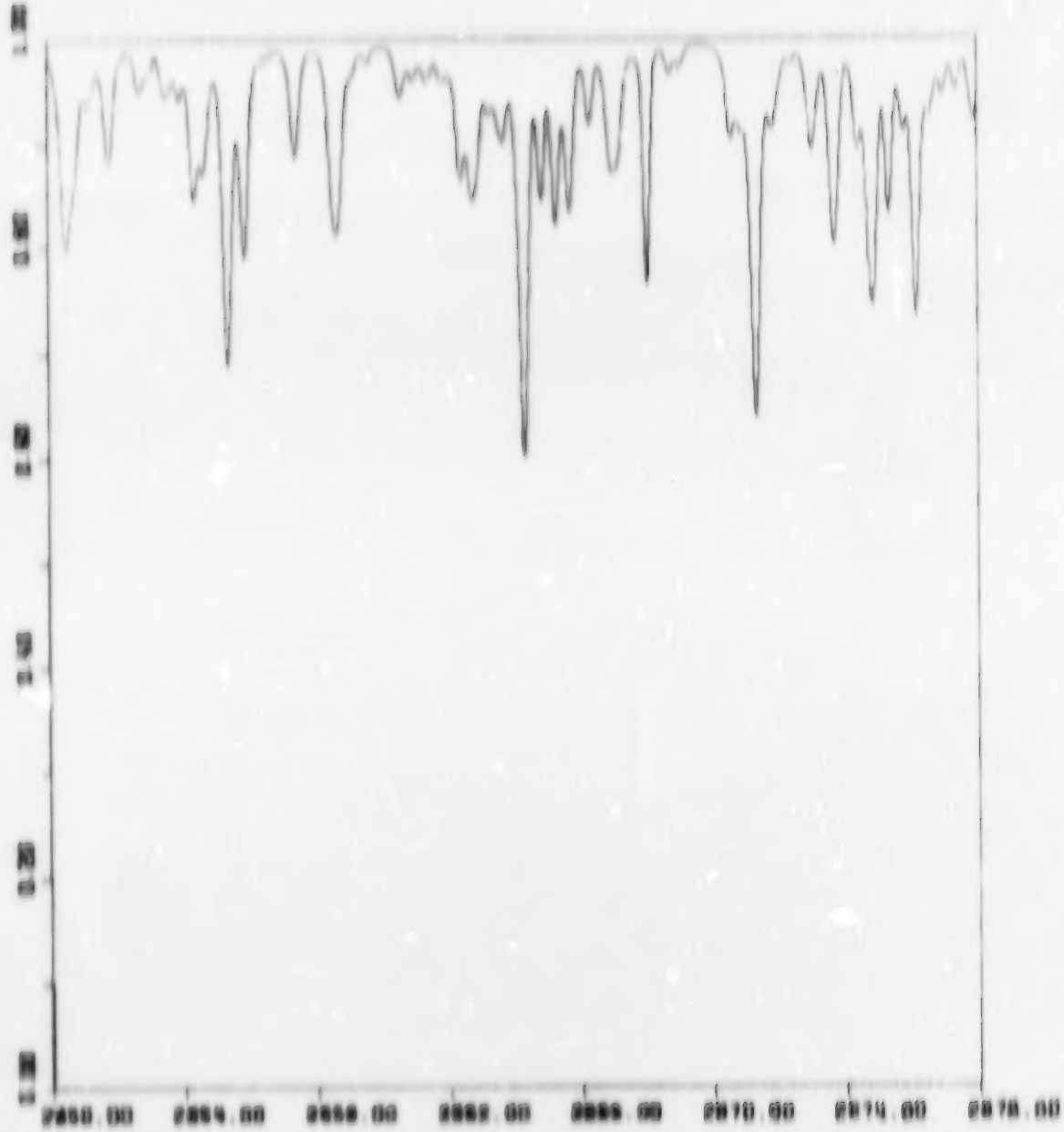
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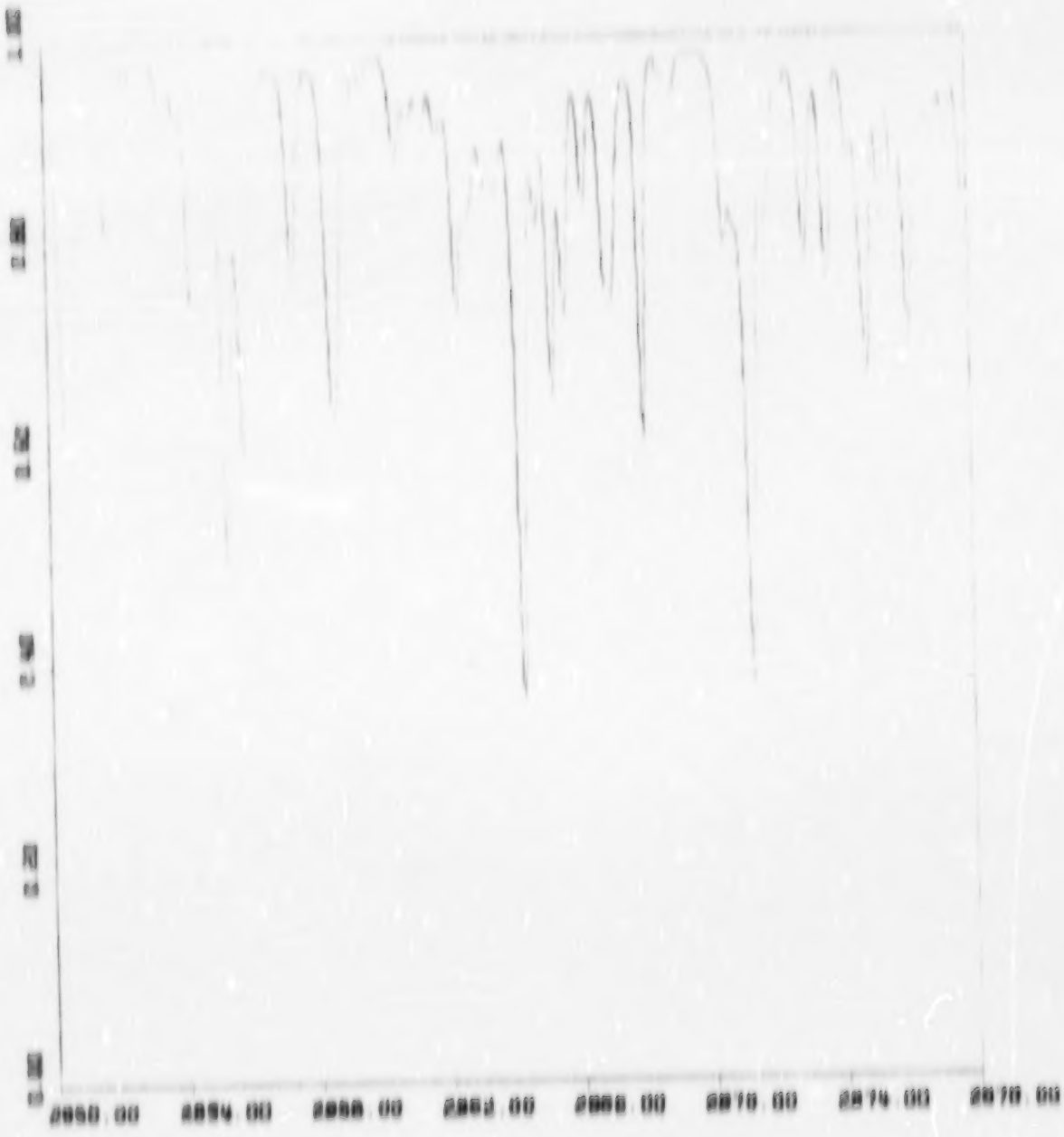
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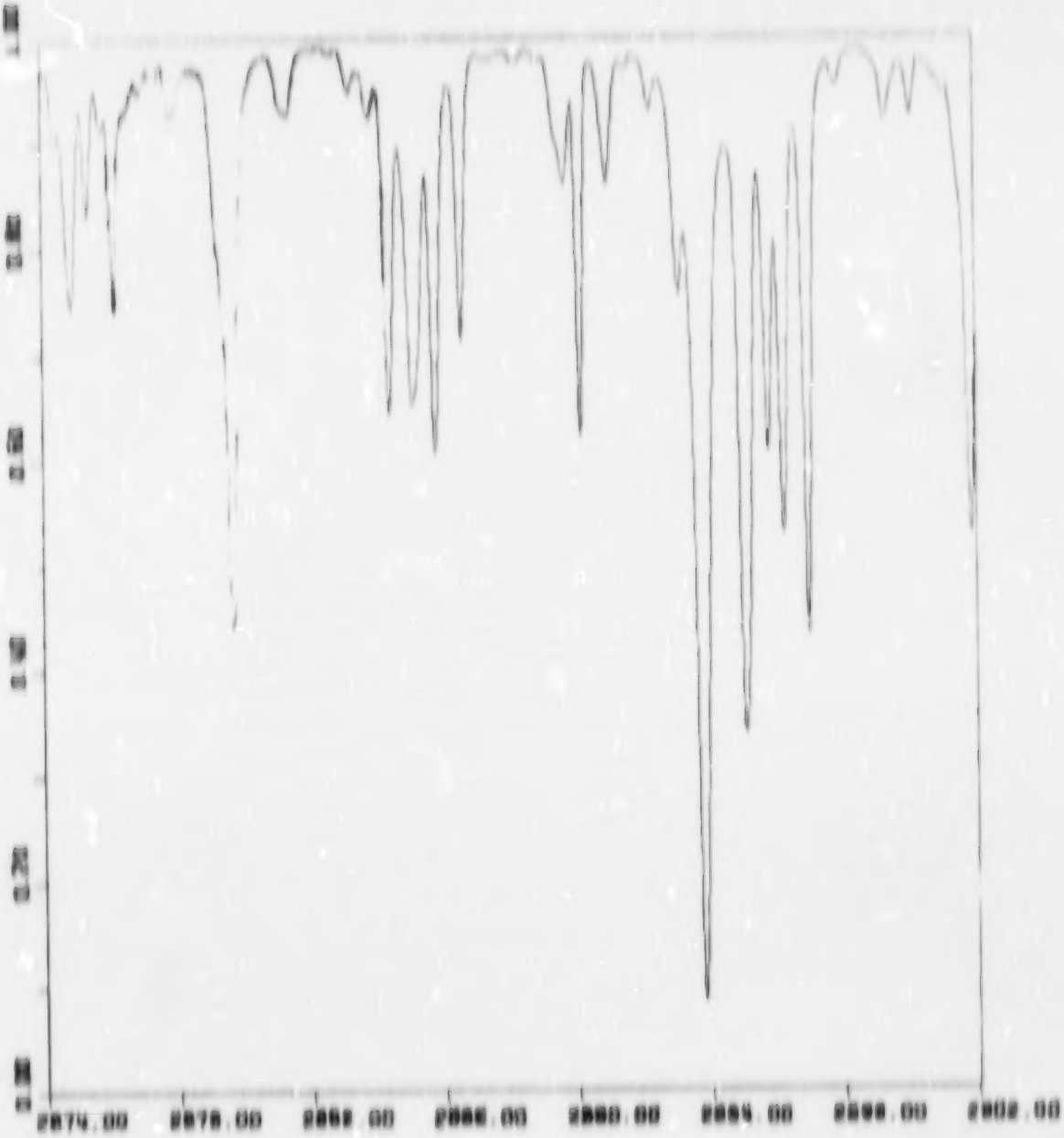
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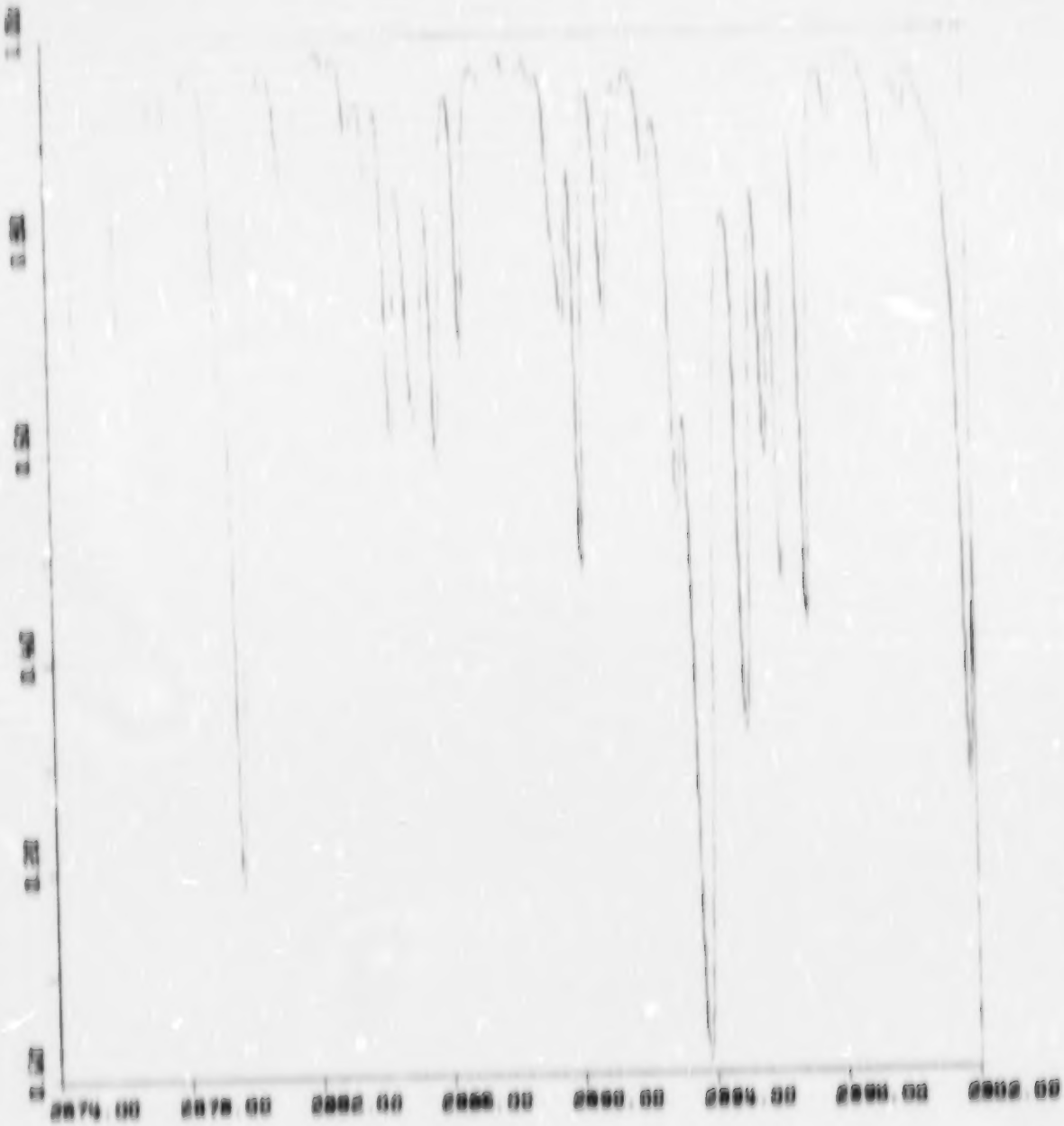

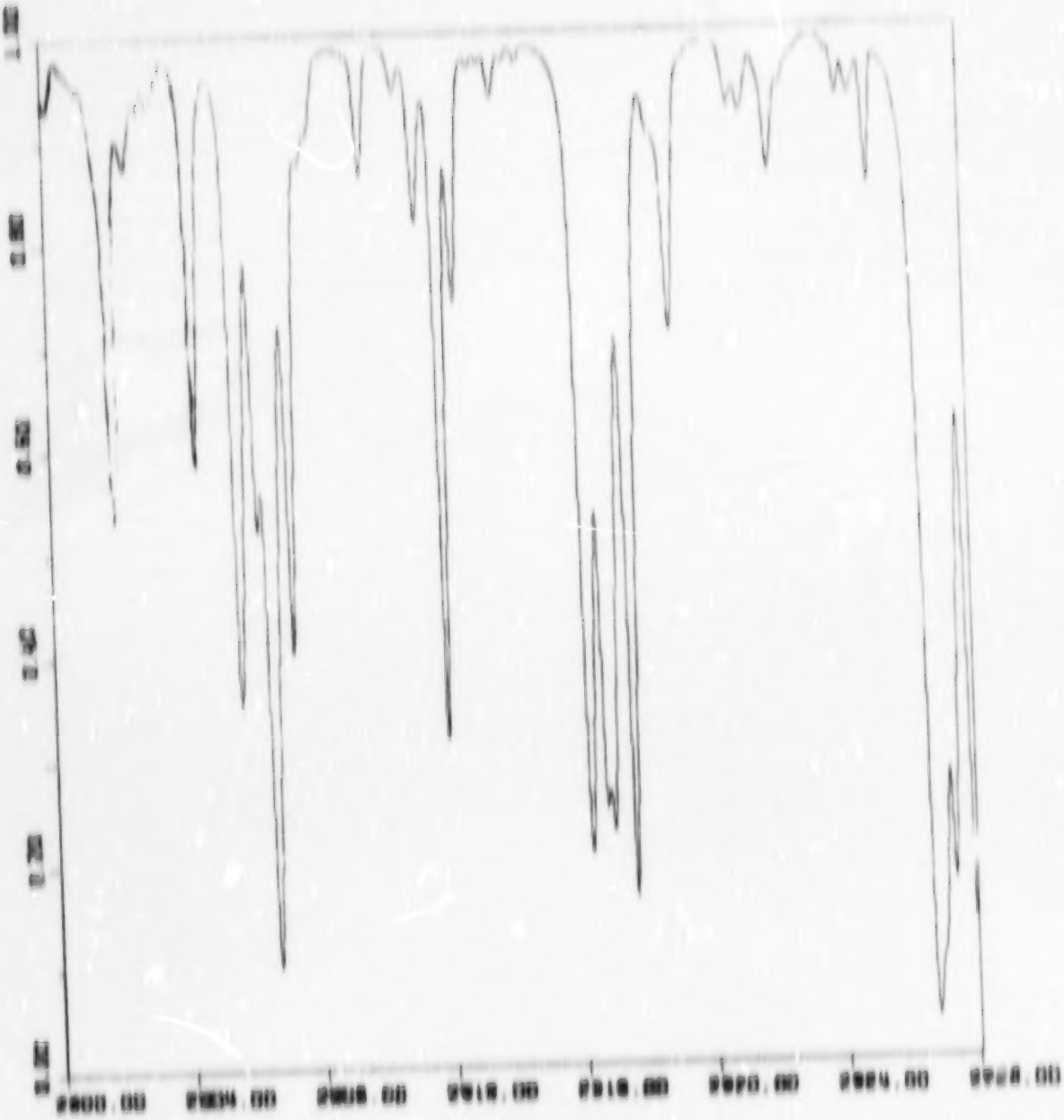

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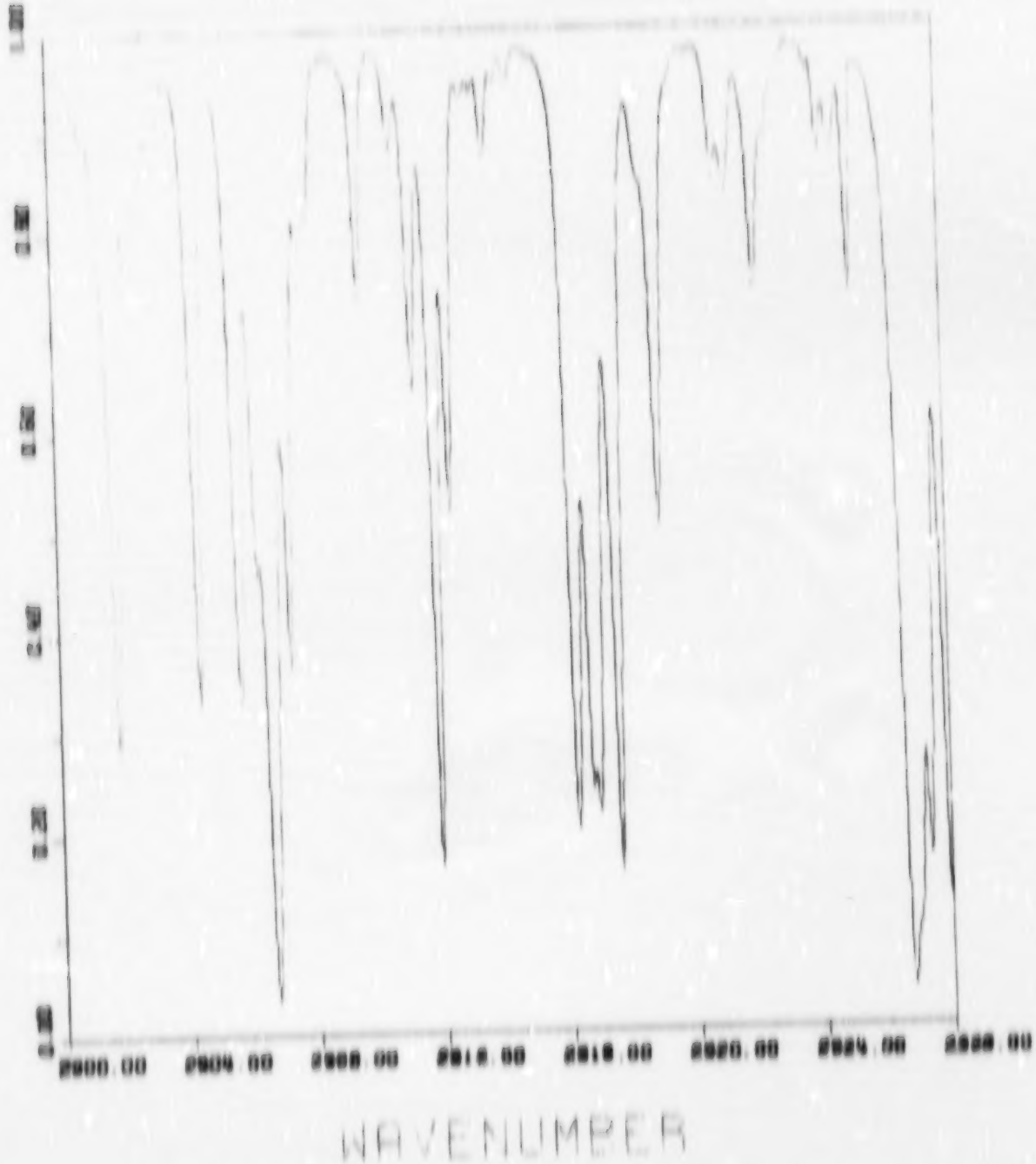
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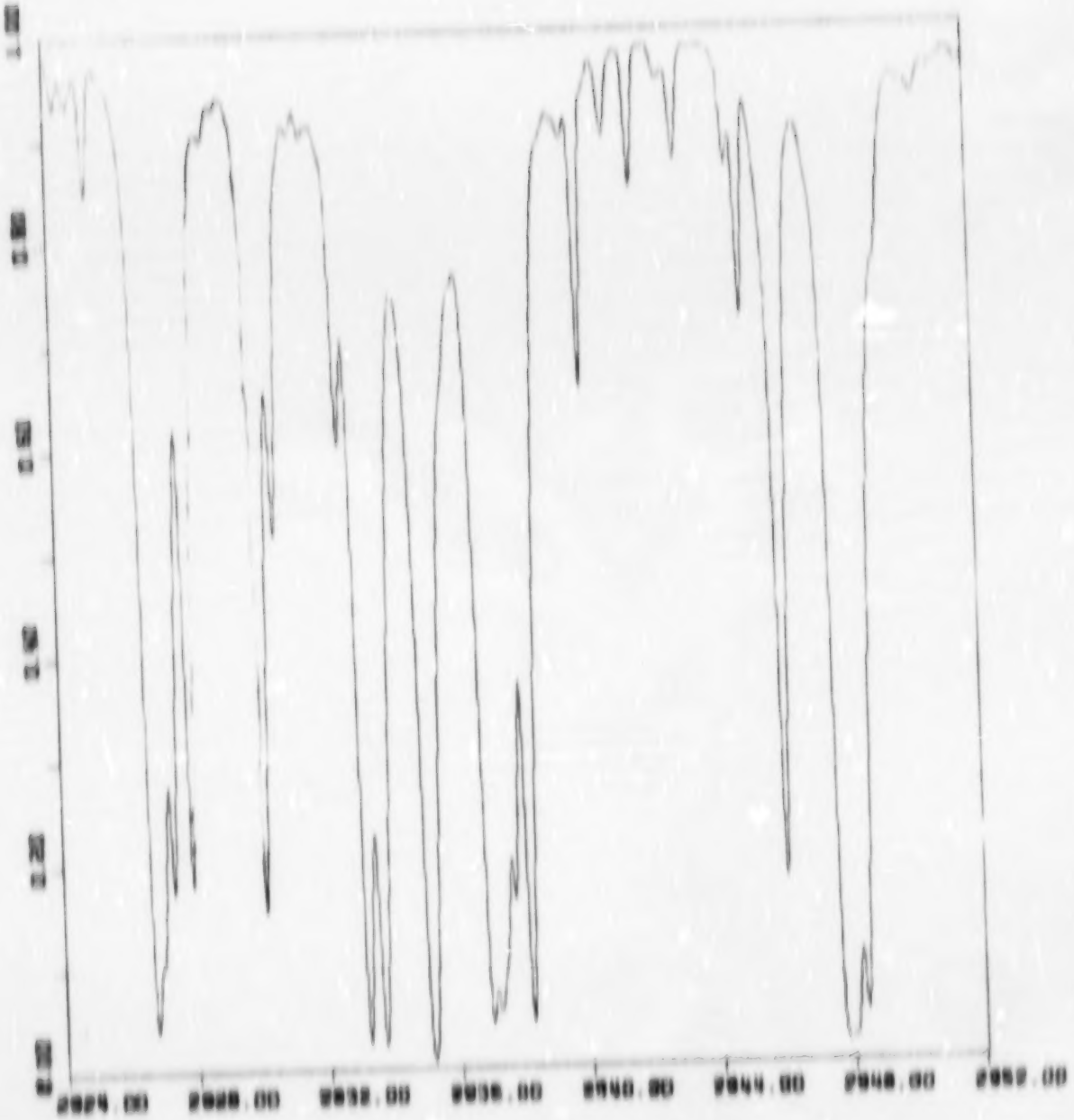
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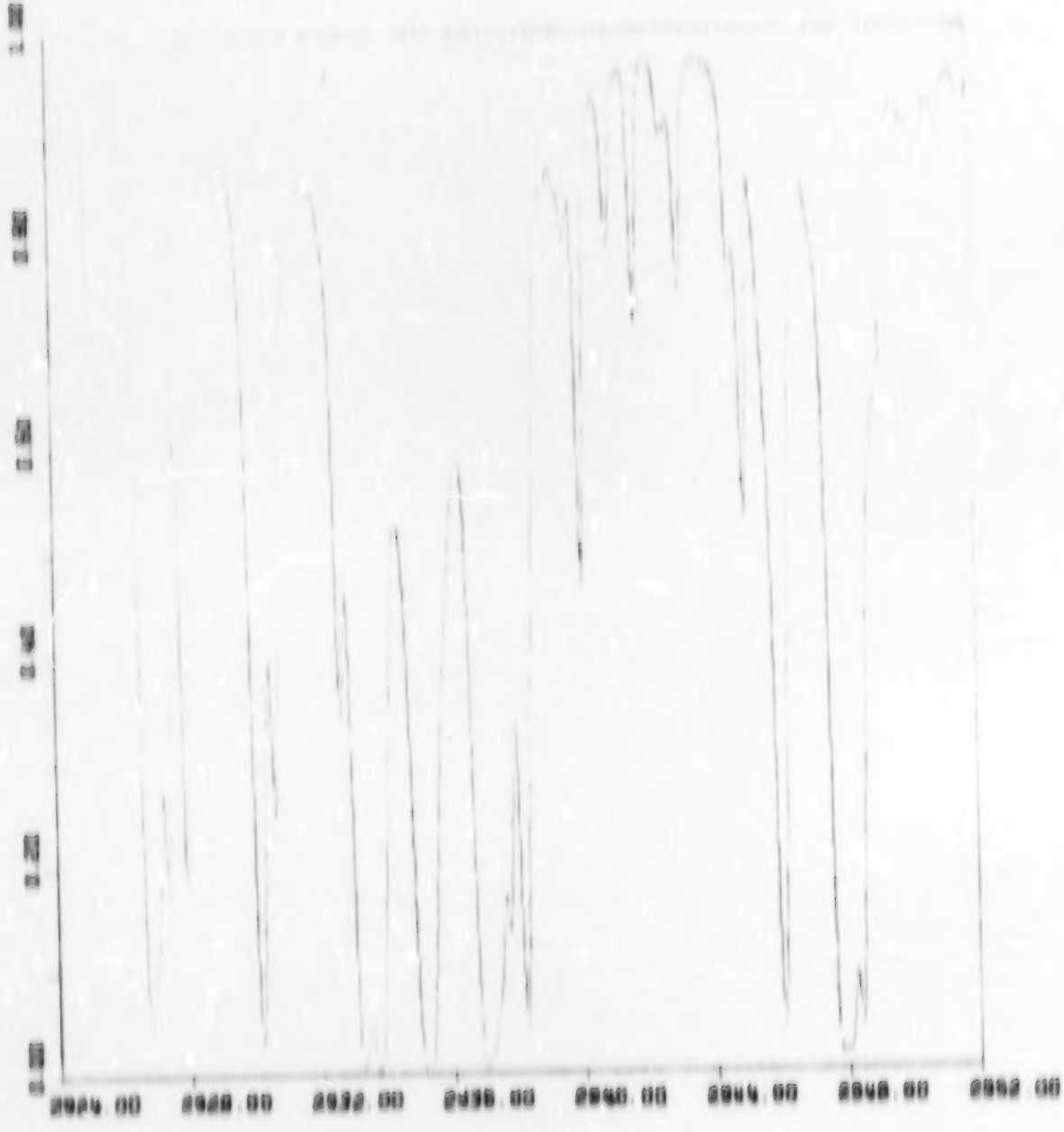

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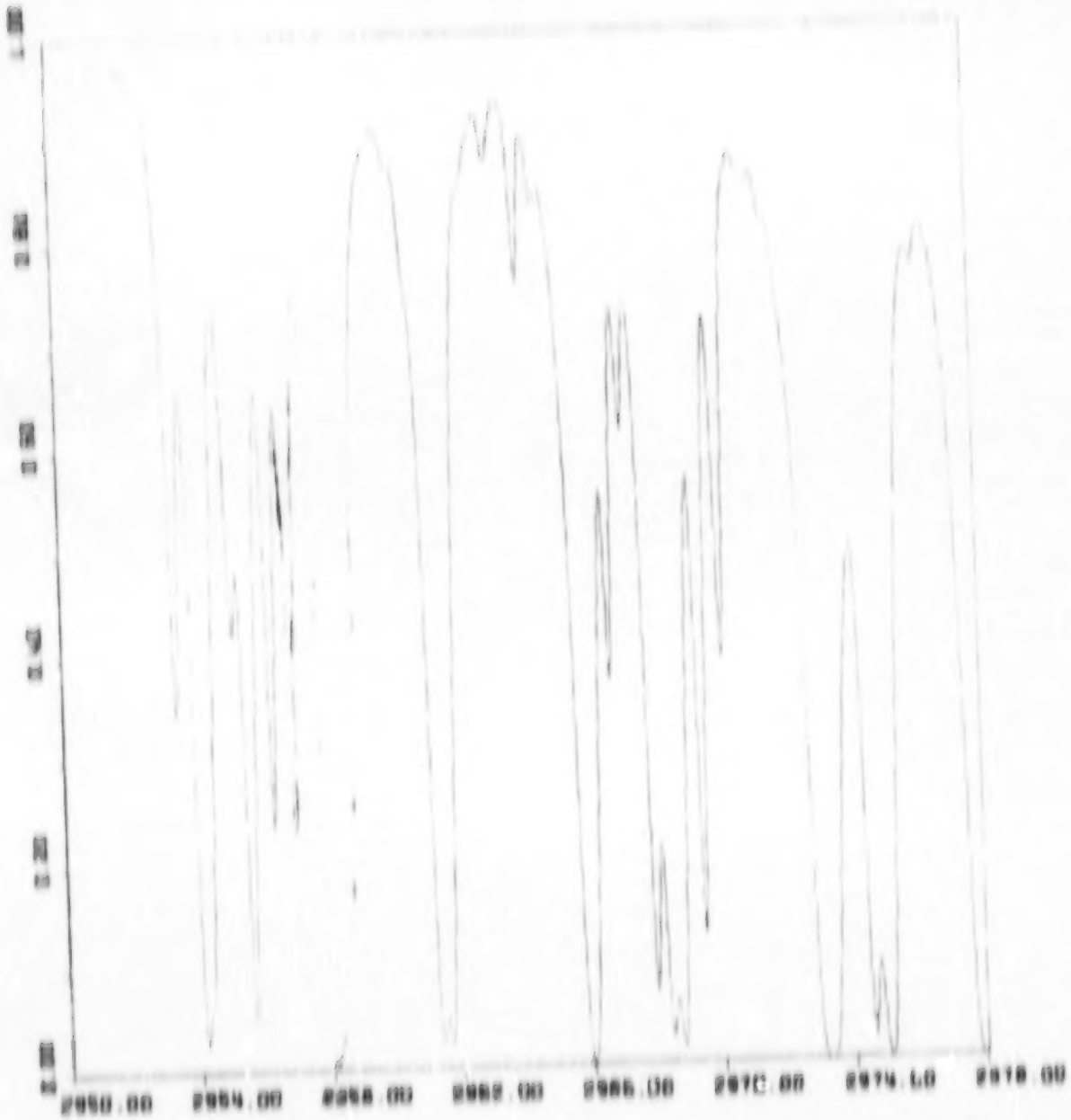
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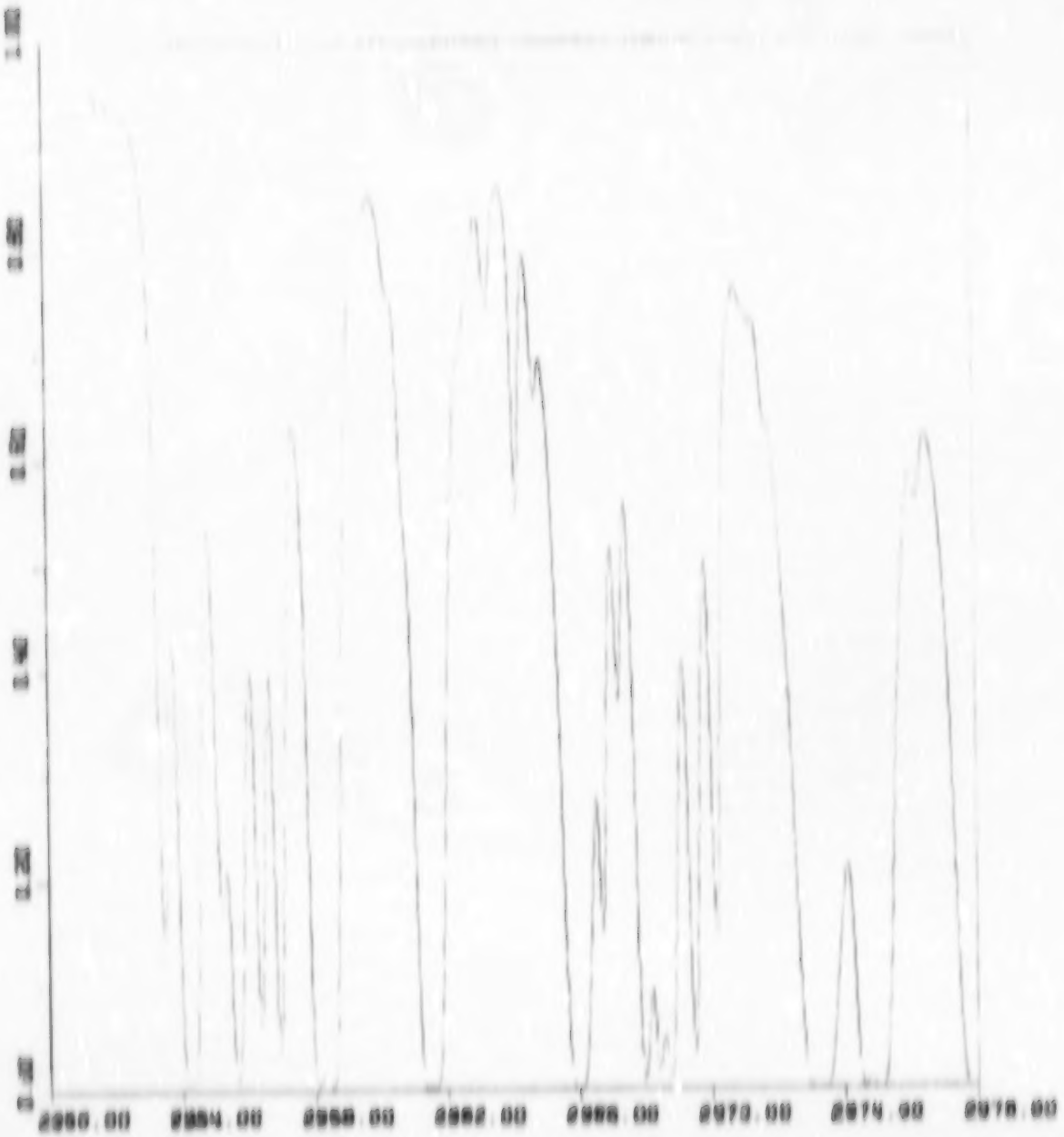
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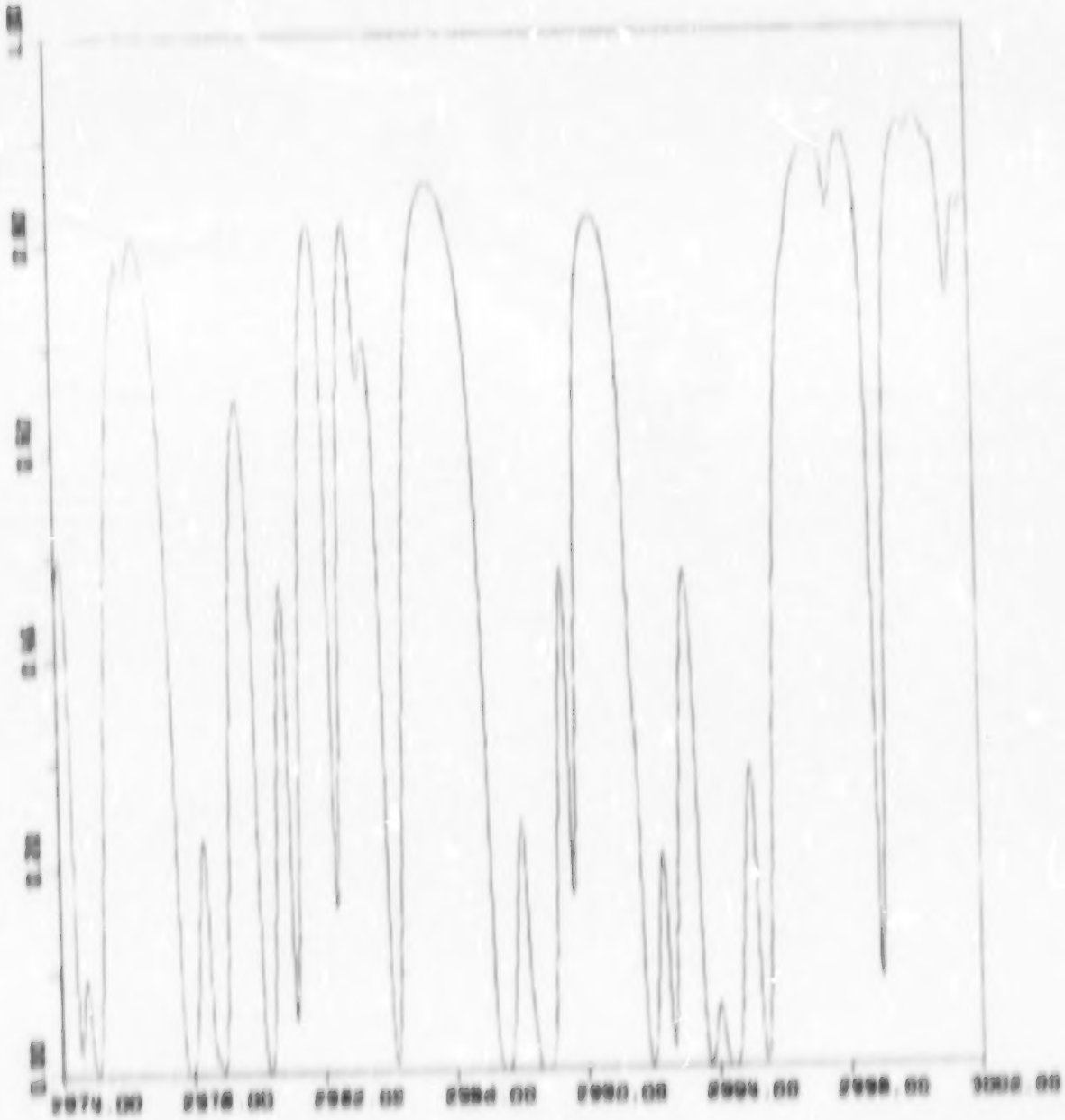
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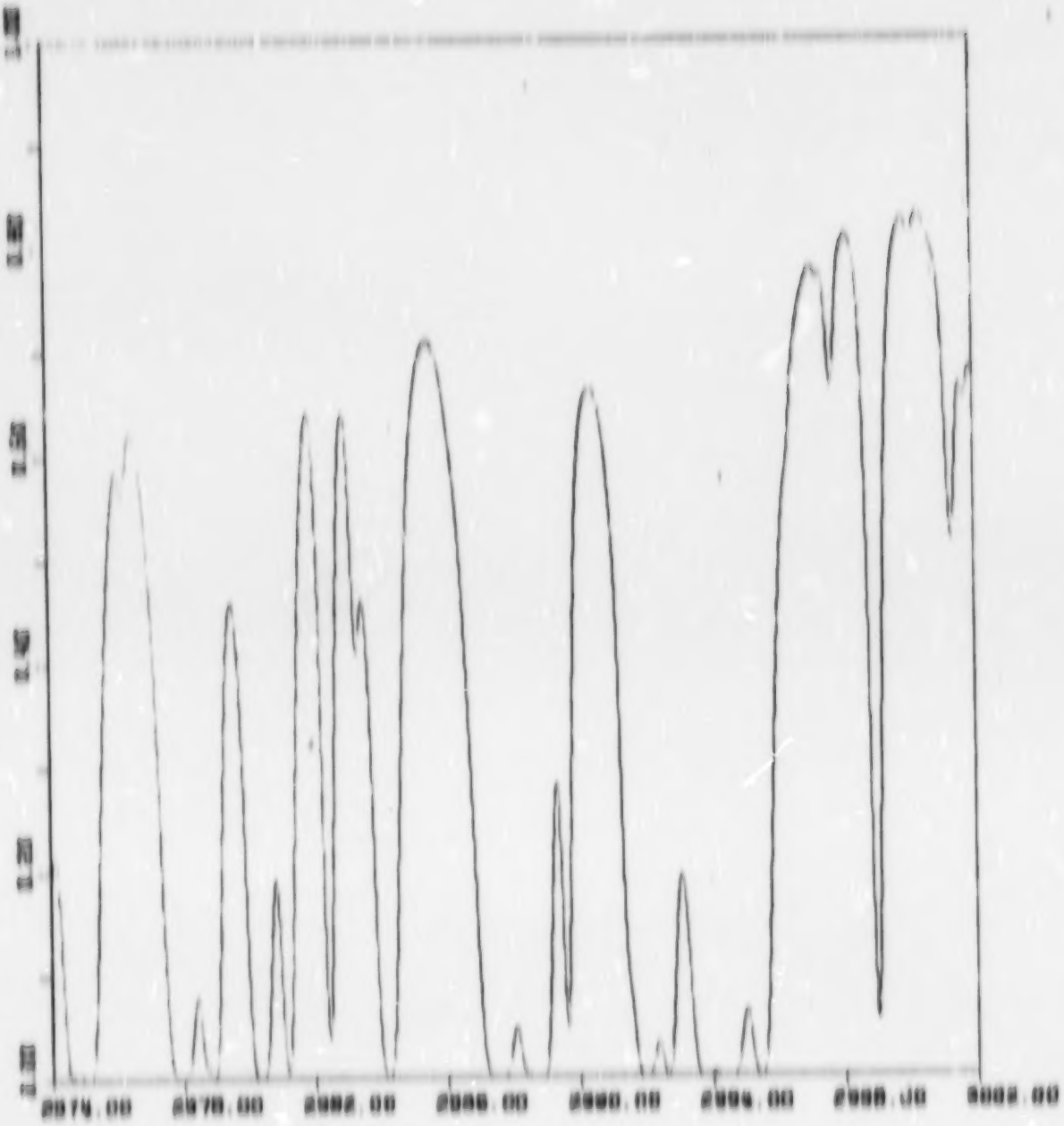
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